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General Electric Co, Philadelphia, PA

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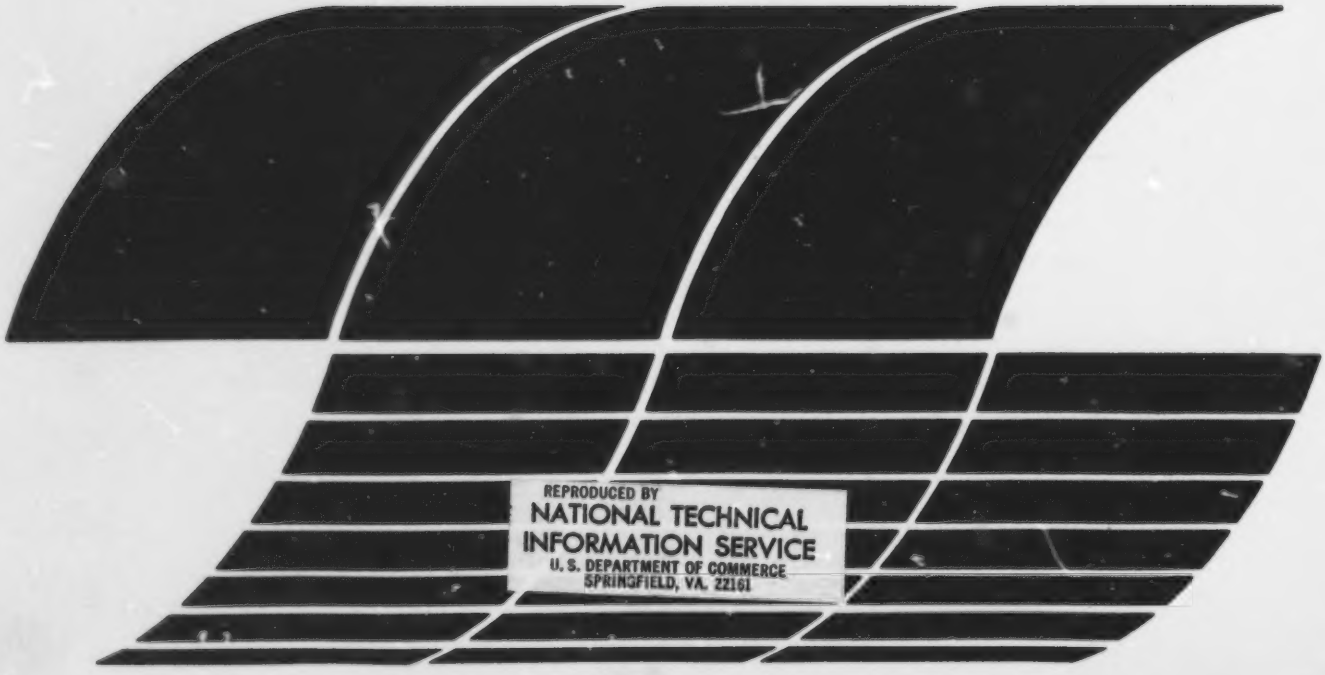

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16. ABSTRACT The report describes the use of microwave energy and NaOH to remove pyritic and organic sulfur from several U.S. coals. Exposure times on the order of 1 minute at 1 atmosphere of inert gas can remove up to 85% of the sulfur with little or no loss in heating value of the coal. Data analysis suggests that sulfur is converted to water soluble sulfides (Na2S, Na2Sx) in the process and that sulfur conversion follows first-order reaction kinetics. The mechanism by which fast rates of desulfurization are accomplished is most probably related to the fast (and to some degree selective) in-depth heating of the bed. The activation of water, FeS2, and NaOH creates local volatilization, high temperature and pressure conditions which accelerate sulfur reactions before the coal has a chance to decompose. It is also quite possible that local non-equilibrium chemistry (as a result of localized discharge sites) plays a beneficial role.

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Pyrite	Stationary Sources	08G,21D
Coal	Pyritic Sulfur	08I
Coal Preparation	Organic Sulfur	07A,07D
Desulfurization		20N
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Coal Desulfurization Using Microwave Energy

by

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ABSTRACT

A method has been developed which removes pyritic and organic sulfur from several U.S. coals. The method utilizes microwave energy alone to remove 50% of the pyritic sulfur; in combination with sodium hydroxide removes more than 95% of the pyritic sulfur and about 60% of the organic sulfur in exposure times of the order of one to three minutes at one atmosphere of inert gas. Additional sulfur is trapped in the ash when coal is burned accounting for almost complete absence of SO_2 in the combustion gases. The process temperature is a modest 250°C - 300°C and the associated loss in the heating value of the treated coal is insignificant.

Analysis of the data suggests that microwave heating in the absence of NaOH converts FeS_2 to FeS_x (where $x \leq 1$), and gaseous sulfur compounds, thus accounting for 50% removal of pyritic sulfur. In the presence of NaOH sulfur is converted to water soluble sulfides (Na_2S_x, $x \geq 1$) at a rate which appears to follow first order kinetics.

The mechanism by which fast rates of desulfurization are accomplished is most probably related to the fast (and to some degree selective) in-depth heating of the bed. The activation of water, FeS_2 and NaOH create local volatilization high temperature and pressure conditions which accelerate sulfur reactions before the coal has a chance to decompose. It is also quite possible that local non-equilibrium chemistry as a result of localized discharge sites plays a beneficial role.

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SECTION 1

INTRODUCTION AND BACKGROUND

STATEMENT OF PROBLEM

Coal is a plentiful resource asset in the United States and increased use of coal is vital to satisfy the nation's energy needs as well as improve its economic stability and energy self-sufficiency. Despite the vast coal reserves, however, troublesome environmental problems arise from the constituent high-sulfur which, upon combustion, releases sulfur dioxide into the atmosphere.

In accordance with the Clean Air Act of 1970, the Environmental Protection Agency in 1971 promulgated new source performance standards that limited sulfur oxide emissions from coal combustion to 1.2 lb $SO_2/10^6$ Btu. For a 12,000 Btu/lb coal, the above standard limits the coal sulfur content to a maximum of about 0.7% by weight. Thus, the Clean Air Act virtually eliminates direct use of most Eastern and Midwestern coals, which tend to have higher sulfur contents than the Western coals. This becomes a very important consideration because the Eastern and Midwestern coals are closest to the region of maximum need and represent about 40 percent of total U.S. reserves (1,2).

TYPES OF SULFUR IN COAL

Sulfur exists in coal in the "pyritic", "organic", and "sulfate" form. The sulfate sulfur is usually in quantities less than 0.05% and therefore is not an important factor. Pyritic sulfur is present in the form of a dispersion of particles that have the chemical composition FeS_2. The size and form of these particles varies greatly with geographic location, from seam to seam for a specific geographic location, and even within a chunk of coal. The organic sulfur is chemically bound to the organic structure of the coal and accordingly it cannot be removed by conventional cleaning or preparation processes, but requires chemical treatment.

Although there is no exact knowledge of the forms in which organic sulfur is present in the coal matrix, several groups have been suggested. These include disulfides, mercaptans, thioethers and thiophenes. It is also believed that a significant portion of organic sulfur is a part of the heterocyclic aromatic ring structure.

In general, the fraction of the sulfur present in the various proposed forms is unknown. This is indeed unfortunate because the nature of the sulfur compounds involved plays a significant role in terms of identifying an effective desulfurization treatment. It is known for example that sulfur present in the form of ring structures is more difficult to hydrogenate or to remove by thermal decomposition than other forms of organic sulfur. In fact, when coal is coked, as much as 45% of the original organic sulfur remains in the final coke product and it is believed that it is the sulfur in the ring structure which resists removal even at the high coking temperatures. Based on this kind of information it is estimated that 40-60% of the organic sulfur in U.S. coals is present in ring structure.

CANDIDATE DESULFURIZATION PROCESSES

Many methods have been considered for the removal of sulfur from coal (3). Those which have received the most serious attention remove pyritic sulfur using either density difference or magnetic separation techniques (4,5) and chemical desulfurization. The former techniques are only partially effective, limited to inorganic sulfur present largely as iron pyrite, and can result in large heating losses because much useful coal material is carried over with the pyrites. Chemical cleaning methods are more effective in sulfur removal, and fuel value losses can be small; thus, chemical cleaning is now emphasized as having the potential of providing more effective means for coal desulfurization and opening the road towards wider coal utilization.

Among a number of chemical desulfurization methods that have been proposed, three have been actively developed in recent years. These are the TRW-Meyers, the Battelle "Hydrothermal", and the Ledgemont Processes. Brief summaries of these processes are of value.

In the TRW-Meyers process, inorganic sulfur is extracted from small-particle-size coal with a hot solution of ferric sulfate, which is capable of oxidizing pyritic sulfur to soluble sulfates and elemental sulfur (6-10). Since the elemental sulfur is deposited within the coal matrix, a second treatment stage is required to remove the elemental sulfur, either by extraction with an aqueous acetone solvent or alternately by heating and vaporization. Since the leaching step reduces ferric sulfate to ferrous sulfate, the spent leachant is regenerated by re-oxidizing the ferrous sulfate back to ferric sulfate with air or pure oxygen. It is claimed that this process removes practically all the pyritic sulfur present without affecting the heating value of the coal itself. A single batch of homogeneous coal requires a reaction time on the order of eight hours to remove 80% of the pyritic sulfur, although multi-stage leaching can remove considerably more pyrite. This process is the most developed of the candidate chemical methods. It has been evaluated extensively through laboratory and bench-scale testing and has reached the pilot plant demonstration stage.

The Battelle "Hydrothermal" process involves leaching pulverized coal with hot caustic solutions that extract most of the inorganic sulfur and part of the organic sulfur in the form of a soluble sodium sulfide (11-13). If the leached coal is treated subsequently with dilute acid, the ash content is also reduced. Experiments in small laboratory-scale batch and continuous-flow

reactors indicate needed reaction times of about 30 minutes at temperatures up to 350°C and pressures of about 200 atmospheres. The main advantage of this process is the ability to attack both pyritic and organic sulfur without significantly reducing the calorific value of the treated coal.

The Ledgemont process, announced in 1974 (14-16) by Kennecott Copper Corporation, involves leaching pulverized coal with a hot aqueous solution containing dissolved oxygen under pressure. This solution results in oxidation of the iron pyrites and their conversion into sulfuric acid and/or water-soluble sulfates. The most attractive feature of this process is the need for only oxygen and water for leaching out large amounts (90%) of pyritic and modest amounts (20%) of organic sulfur. A major disadvantage, however, results from the loss of about 14% carbon during treatment. Also, the treated coal is significantly inferior in terms of residual heating value (5-15% loss) (17).

Further tests with this process using compressed air instead of oxygen in the range of 35 to 100 atmospheres of pressure, and temperatures in the vicinity of 200°C have been conducted at Pittsburgh Energy Research (DOE-Lab) with interesting results (18). Most of the pyritic sulfur (90%) and up to 40% of the organic sulfur in coal are converted into sulfuric acid, with an overall heating value recovery of 93 to 97% in small-scale laboratory experiments. Apparently, the higher temperatures result in the extraction of part of the organic sulfur.

Even though the Ledgemont-type processes appear promising for chemical desulfurization, they are limited by relatively slow rates of sulfur extraction, the presence of relatively corrosive dilute sulfuric acid solutions, and the need for operation at relatively high pressures.

Other desulfurization methods that deserve mention include the IGT-Hydrodesulfurization process, the Syracuse Corporation's chemical comminution process and the Hazen process.

The IGT process (5) uses pre-oxidized coal, hydrogen at modest pressures, and temperatures as high as 800°C. The process removes 80-90% of pyritic sulfur and 60-80% of organic, but causes excessive volatilization of the coal and losses of solids as high as 38% of the original weight. (In order to satisfy EPA requirements, both gas and solid phases have to be used.)

The Syracuse process, developed by Howard (20), involves chemical comminution of coal by use of liquid ammonia at high pressure. It breaks up the matrix and enhances the detachment of mineral matter; thus, separation by gravity is improved.

The Hazen process claims a selective chemical reaction of the mineral component in pulverized coal with gaseous iron pentacarbonyl which converts the pyritic sulfur into a paramagnetic substance without affecting the mineral-free coal. The magnetic mineral component is subsequently separated from the pulverized clean coal by dry magnetic separation methods. The process is limited to removal of pyritic sulfur only and severe grinding will be required for many Eastern coals which contain very fine size pyrites ($\sim$50

micron mean diameter). Iron pentacarbonyl [$Fe(CO)_5$] consumption of about 32 lbs/ton of coal is required (21) as well as severe monitoring requirements are expected because of the very high toxicity of iron pentacarbonyl. The distinct advantages of the process are associated with the moderate temperature, low pressure and relatively short retention time requirements.

SECTION 2

THERMOCHEMISTRY

THERMAL DECOMPOSITION

As previously discussed sulfur in coal is strongly bonded either to iron (Fe-S) or to carbon (C-S), with bond energies of 115 and 175 kcal/mole respectively. For this reason, it is difficult to break these bonds thermally without partially decomposing the coal matrix itself.

When coal is heated to temperatures in excess of 400°C it is known to enter a regime of thermal decomposition which eventually removes most of the hydrogen in the form of H_2 and hydrocarbons and greatly reduces the heat content of coal. Figure 1 shows mass spectrometric data as a function of temperature of species emanating from Clarion County, Pa. coal (containing 4.1% sulfur, mostly pyritic). The sample was heated in a tantalum crucible in a conventional furnace at a heating rate of 10°C/min. using the time-of-flight mass spectrometer apparatus as described in previous publication (24). It is apparant from these data that the evolution of sulfur compounds (H_2S, SO_2, SO, or CH_3SH and COS) is essentially coincident with the evolution of hydrocarbons (all observed species are not shown on this plot). At the end of such a run, 30-35% of the weight is lost because of the generation of volatiles, while a significant portion of the sulfur still remains in the charred residue. It is for this reason that reactants such as O_2, H_2 and NaOH have been considered (for the removal of sulfur) in the hope that sulfur can engage in reactions which remove it from the coal matrix without seriously decomposing the coal itself.

REACTIONS OF PYRITIC SULFUR WITH LEACHANTS

Thermochemical Calculations

Nepokrytykh et.al. (22) have treated pyrite with alkali solutions in the vicinity of 300°C in an autoclave. The sulfur is extracted by the solution as $S^=$ (90-93%) and as $S_2O_3^=$, $SO_3^=$ and $SO_4^=$ (total 7-10%). The solid phase undergoes the following sequence of transformation:

$$\underset{FeS_2}{\text{pyrite}} \longrightarrow \underset{Fe_2O_3}{\text{hematite}} \longrightarrow \text{maghemite} \longrightarrow \underset{Fe_3O_4}{\text{magnetite}}$$

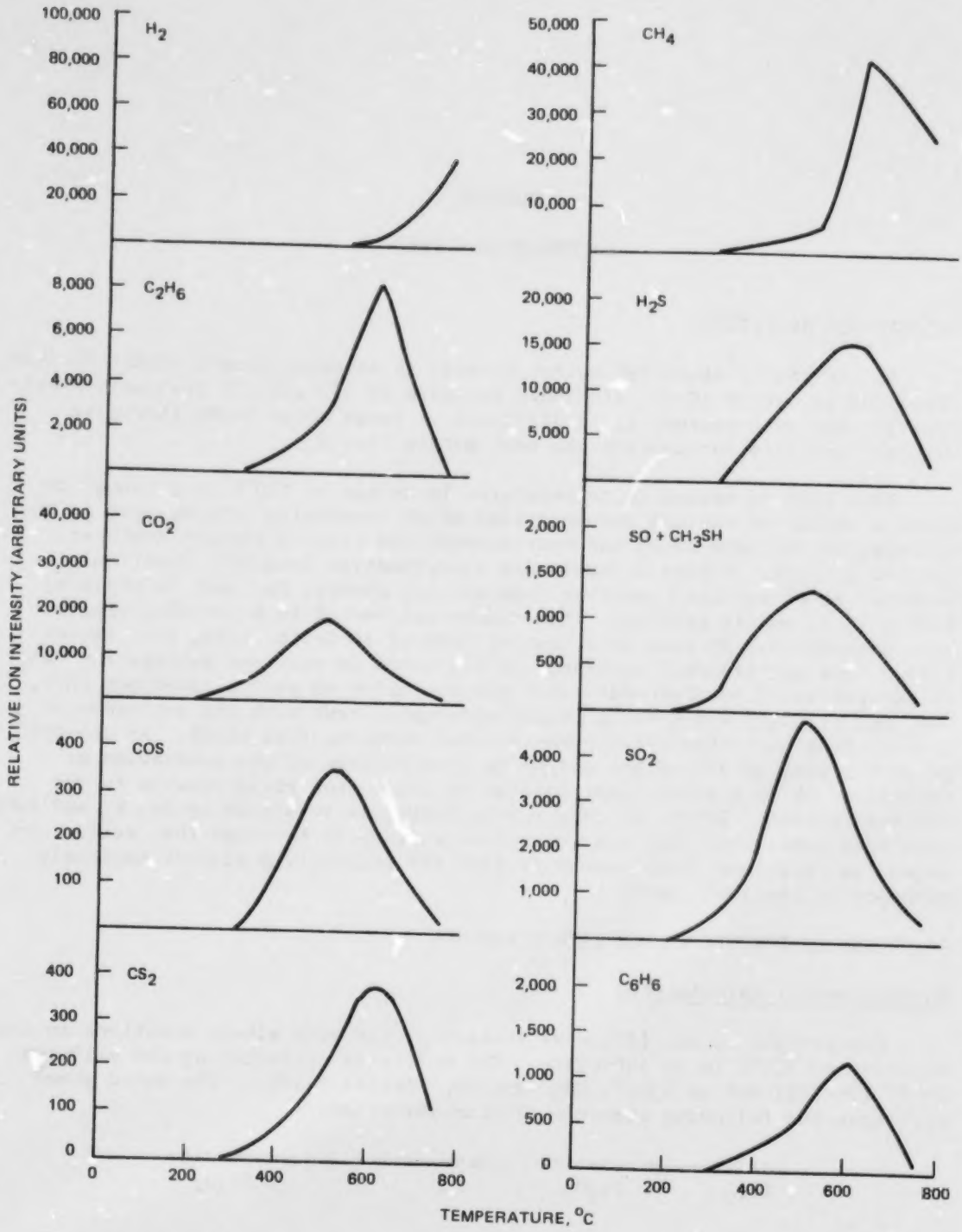


Figure 1. Mass spectrometric analysis of gaseous products from coal.

This process can be represented to a first approximation as follows:

$$FeS_{2(s)} + 4NaOH_{(s)} \longrightarrow \left(\frac{32}{35}\right)\left[\left(\frac{1}{2}\right) Fe_2O_{3(s)} + 2\ Na_2S_{(s)} + 2H_2O_{(1)}\right] + \left(\frac{3}{35}\right)\left[\left(\frac{1}{3}\right) Fe_3O_{4(s)} + 2\ Na_2SO_{4(s)} + 2H_{2(g)}\right] \quad (2)$$

The free energy and enthalpy changes for reaction (2) as a function of temperature using the thermochemical data of Barin (23) are as follows:

	T (°K)		
	400	500	600
ΔF^o (kcal/mole FeS_2)	0.7	-2.4	-3.8*
ΔH^o (kcal/mole FeS_2)	10.5	11.4	0.4*

It is noteworthy that the heat of solution of Na_2S in $H_2O_{(1)}$ will alter the numerical values computed for ΔF^o and ΔH^o.

From NBS Circular 500 (Part 1 Tables - pp.456-7), "Selected Values of Chemical Thermodynamic Properties", (1952), the following considerations help evaluate the FeS_2/NaOH system:

Species	State	$\Delta H_F^o{}_{298}$
Na_2S	Condensed	- 89.2
$Na_2S \cdot 4\frac{1}{2}H_2O$	Condensed	-416.9
H_2O	Liquid	- 68.32

Therefore,

$$Na_2S_{(c)} + 4\tfrac{1}{2}H_2O_{(1)} \longrightarrow Na_2S \cdot 4\tfrac{1}{2}H_2O_{(c)}$$

$$-89.2 \quad (4\tfrac{1}{2})(-68.32) = -307.44 \quad -416.9$$

$$\Delta H = -416.9 + 396.64$$

$$= -20.26 \text{ kcal/mole of hydrated } Na_2S$$

and $$\Delta H_R^{**} = \left(\frac{32}{35}\right)\left(-20.26\right)\left(\frac{2}{4.5}\right) = -8.22 \text{ kcal/mole}$$

* NaOH in a liquid at 600°K

** Change in heat of reaction (2) due to hydration

The exothermic heat of hydration of Na_2S should be sufficient to drive the ΔF for the pyrite + NaOH reaction negative.

If we assume Na_2S hydrates to $Na_2S(4\frac{1}{2}H_2O)$ we should add -8.22 kcal/mole to the previous table which makes reaction (2) exothermic even at 600°K (327°C).

Finally, 8.6% (3/35) of the hydrogen in the reaction is released as gaseous hydrogen; it is important to know whether this H_2 is reabsorbed in the coal matrix.

If NaOH is substituted with Na_2CO_3 the corresponding reaction can be represented, to a first approximation, as follows:

$$FeS_{2(s)} + 2Na_2CO_{3(s)} \rightarrow \left(\frac{32}{35}\right)\left[\frac{1}{2}\ Fe_2O_{3(s)} + 2Na_2S_{(s)} + 2CO_{2(g)}\right] + \left(\frac{3}{35}\right)\left[\frac{1}{3}\ Fe_3O_{4(s)} + 2Na_2SO_{4(s)} + 2CO_{(g)}\right] \quad (3)$$

The free energy and enthalpy changes for reaction (3) as a function of temperature using the thermochemical data of Barin (23) are as follows:

	T (°K)		
	400	500	600
ΔF^o (kcal/mole FeS_2)	56.5	47.4	40.9
ΔH^o (kcal/mole FeS_2)	92.4	88.8	88.6

Since the free energy change for reaction (3) is a large positive value the use of Na_2CO_3 as a leachant (for sulfur) is not favored thermodynamically.

Other candidate reactions of interest include the use of O_2 and H_2. In the case of O_2 substantial oxidation of the coal matrix has been observed under conditions of sulfur oxidation. The use of H_2 produces H_2S under conditions of temperature and pressure where considerable amount of coal is decomposed (5).

Experimental Data on Pyrite Reactions

In an effort to gain some basic understanding on the behavior of FeS_2 as a function of temperature and the presence of reactants (which may hold promise in coal desulfurization), a series of measurements were made on the gaseous species using the Knudsen Crucible/Time-of-Flight Mass Spectrometer apparatus.

The first series of experiments involved heating FeS_2 in the same manner as coal was heated in gathering the data shown in Figure 1. The reported ion intensity as a function of temperature as shown in Figure 2 reveals the behavior of pyrite. At a temperature close to 400°C under conditions of equilibrium pyrite begins to decompose and releases gaseous sulfur. The most abundant vapor species are S_2, S_3, S_6, S_7, S_8, and S_5.* The decline in ion intensity at temperatures above 700°C suggests the depletion of sulfur in the sample due to the conversion of FeS_2 to FeS.

In order to distinguish between FeS_2 vaporization and FeS_2 oxidation, oxygen was added to the crucible. The results of this experiment are shown in Figure 3. The major peaks observed were mass 64 due to S_2 and/or SO_2, 48 due to SO, and 80 due to S_2O. This experiment suggests that the formation of the sulfur oxides coincides with the evolution of elemental sulfur from the decomposition of FeS_2 and also with the thermal decomposition of coal itself (see Figures 1 and 2). This in turn suggests that the use of O_2 under conditions of equilibrium converts sulfur to its oxides in a temperature range which is too high in order to achieve desulfurization without the destruction of coal itself.

The next series of experiments involved heating FeS_2 in the presence of NaOH. The ratio of FeS_2 to NaOH was 3.76 (by weight) which resulted in an excess of FeS_2 in terms of the stoichiometry required to form Na_2S (i.e. $FeS_2 + 4NaOH$).

The results of these experiments are shown in Figure 4. The most striking result from this series is the fact that although FeS_2 was in excess no gaseous sulfur was observed until the temperature reached 650°C. This suggests that FeS_2 has reacted with NaOH at a temperature range well below the decomposition range of FeS_2 (or coal itself) to form the bisulfide Na_2S, and perhaps polysulfides Na_2S_x (where $x>1$). It also suggests that these compounds are stable to relatively high temperatures (600°C or higher). This is an important result because low temperature sulfur reactions are required to bring about chemical desulfurization of coal.

It is obviously important to make similar runs with H_2 as well as replacing FeS_2 with model organic compounds which have been considered to host organic sulfur in coal.

Based on the above discussion, it appears that the ideal chemical desulfurization process is one which maximizes the rates of sulfur removing reactions, while the chemical attack (and the reduction in heating value) of the coal matrix is held at a minimum. This is difficult because both the desulfurization reactions as well as the destruction of coal are favored by increased temperature and the presence of oxidants. Therefore, a method, which is capable of selectively heating or chemically activating regions high in sulfur content and/or selectively heating (or activating) a leachant, is expected to induce non-equilibrium conditions which accelerate rates of reactions involving sulfur bonds, shorten the total reaction time, and reduce energy and pressure requirements. This, in turn, would simplify the process and eventually reduce process costs. The use of microwave energy, as discussed in a later section, appears to hold promise in terms of process simplicity and economics.

* S_5 and S_7 were not plotted.

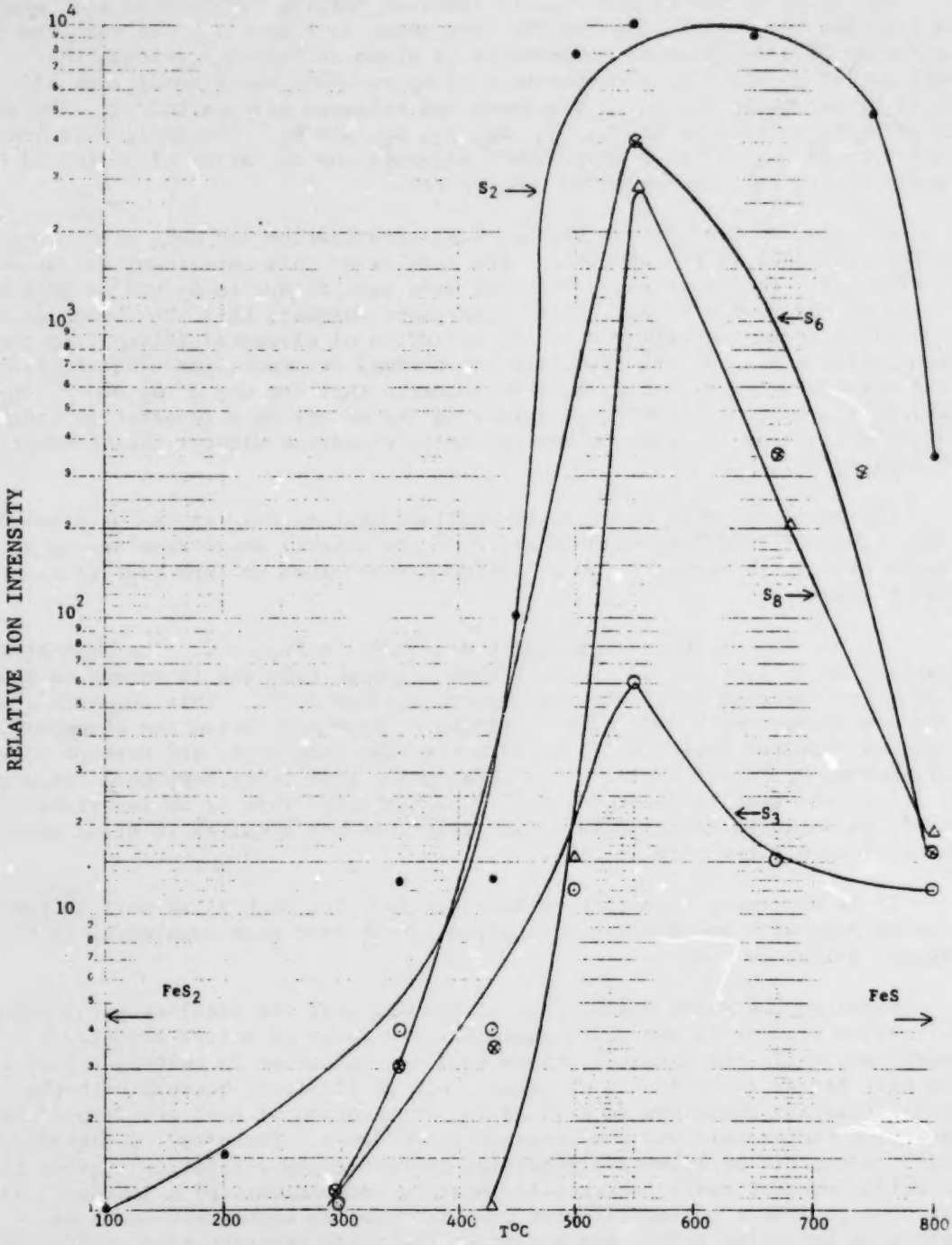


Figure 2. Mass spectrometric analysis of the vaporization of FeS_2.

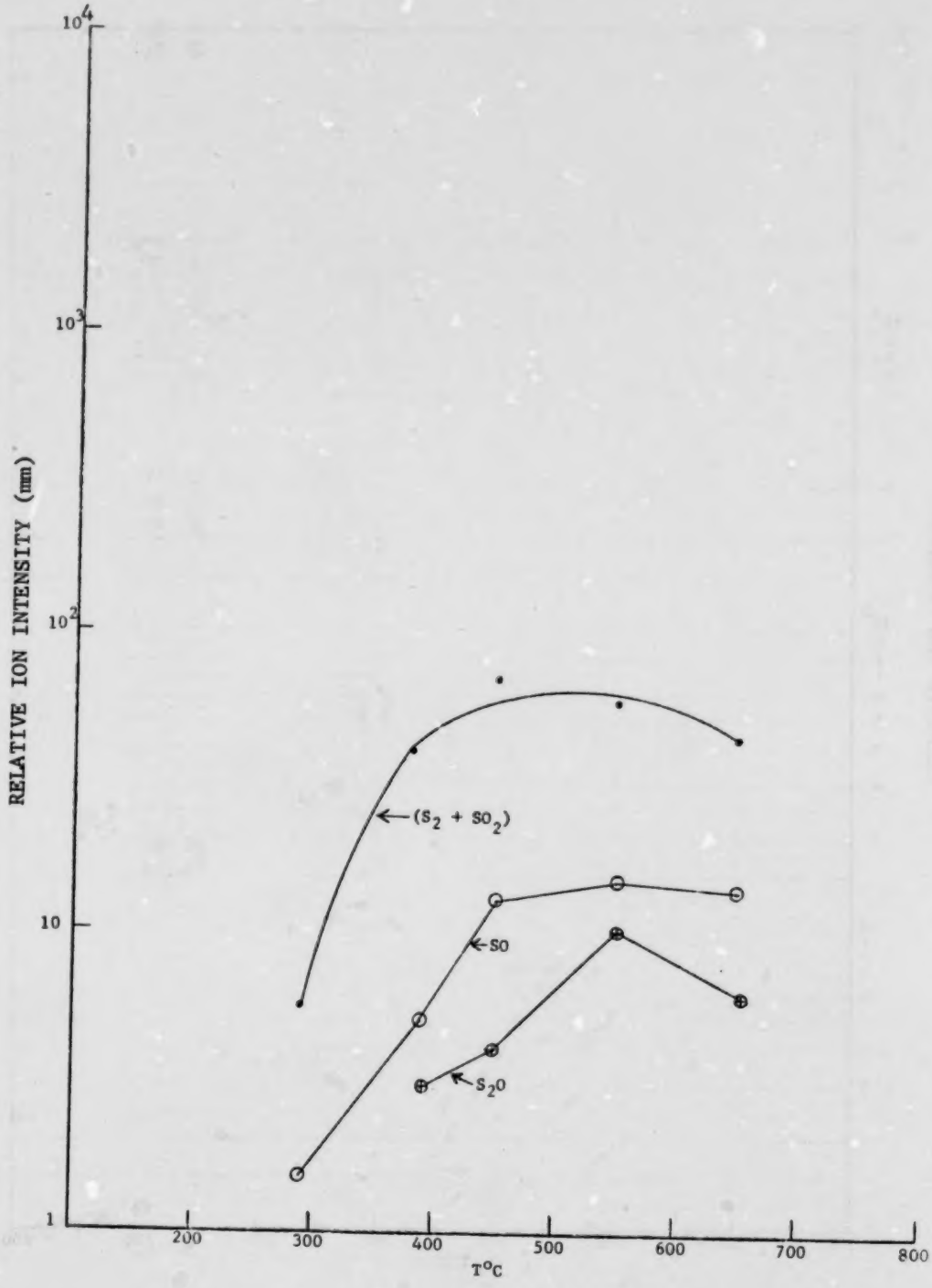


Figure 3. Gaseous products from pyrite oxidation.

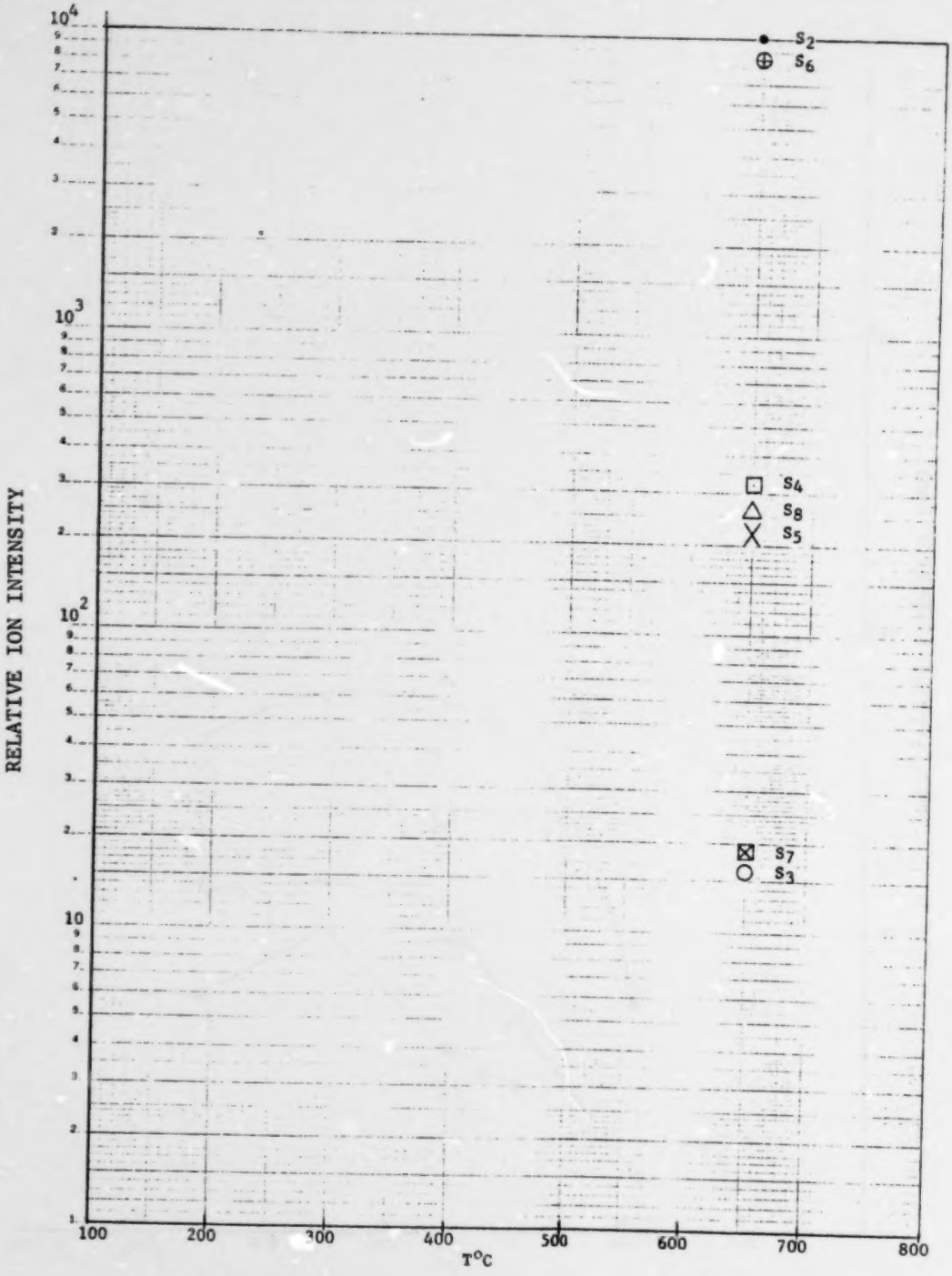


Figure 4. Gaseous products from pyrite reaction with sodium hydroxide.

SECTION 3

THE USE OF MICROWAVES IN COAL DESULFURIZATION

THEORY AND MEASUREMENTS OF DIELECTRIC PROPERTIES

The potential usefulness of microwaves in chemical desulfurization is supported by the physical nature of microwave energy absorption. Microwave power dissipation by a medium is proportional to the imaginary part of the complex dielectric constant (ϵ'') which is a measure of the dissipated power per unit electric field (squared) according to

$$P/V = \pi f \epsilon_o \, E^2 \, \epsilon''$$

where

P is power absorbed

V is volume

f is the applied frequency (1/sec)

ϵ_o is the permittivity of free space (3.85×10^{-12} farads/m)

E is the electric field (V/m)

ϵ'' is the imaginary part of the complex dielectric constant

In the case of inhomogeneous mixtures, if ϵ'' differs significantly within the mixture, one would expect different heating rates and pressure rise within the various regions and most probably a change in the overall chemistry of the system, as compared to a method of heating based on conduction from the exterior of the sample. In the case of polar molecules ϵ'' is high and one can expect a situation whereby the energy is channeled into the medium primarily via molecules of high dipole moment even though these molecules may be uniformly dispersed. Under conditions of high power density (or pulsing) one expects maximum deviations from equilibrium and perhaps the most interesting effects relative to being able to shift reaction rates advantageously.

The work of Ergun and Berman at the Bureau of Mines (25) has demonstrated that pyrites can indeed be selectively heated by microwaves in the presence of coal, and partially converted to para-magnetic forms. This conversion, which takes place in the absence of any observed loss of coal volatiles, was considered beneficial in terms of increasing the efficiency of subsequent magnetic separation of pyrites from coal.

Further studies at this Laboratory directed towards gaining basic understanding of the very complex nature of coal, included measurements on the dielectric properties of coal and some of its significant sulfur compounds such as pyrite (FeS_2), thianthrene ($C_{12}H_8S$), dibenzothiaphene ($C_{12}H_8S_2$), potential leachants such as $NaOH/H_2O$, as well as mixtures of coal/FeS_2 and coal/NaOH with H_2O. The complex dielectric constants were determined from waveguide measurements. These measurements consisted of completely filling a known length of the waveguide with the material and measuring the complex reflected signal, the position of minimum and amplitude of the transmitted signal. The measurements were repeated for various specimen lengths. The apparatus used for these measurements is shown schematically in Figure 5.

Typical microwave transmission measurements are shown in Figure 6 for Ky. #11 coal mixed with a NaOH solution into a slurry. Measurements were made on transmitted and reflected power; absorption was obtained by subtracting the sum of the two from the total incident power.

Furthermore, Figure 7 shows the ratio of absorbed/incident power at 8.3 GHz for several materials media of interest. The apparent conclusion is that coal low in pyrites is relatively transparent to microwaves at this frequency while pyrites (FeS_2) and NaOH (especially with water) greatly enhance the level of absorption.

The complex dielectric constant was varied in a computer program to match the experimental results. Measured dielectric values at 8.3 GHz for compounds of interest are shown in Table 1.

TABLE 1. MEASUREMENT OF COMPLEX DIELECTRIC CONSTANTS AT 8.3 GHz

Material	ϵ'' (Loss)
Coal (Ky. No. 11; Primarily Organic Sulfur)	0.12
FeS_2	1.0
$C_{12}H_8S_2$	<0.01
$C_{12}H_8S$	0.01
NaOH	0.10
NaOH + Coal (Dry)	0.30
NaOH (9.4%) + Coal (59%) + H_2O (31.6%)	1.9
Free Space	0

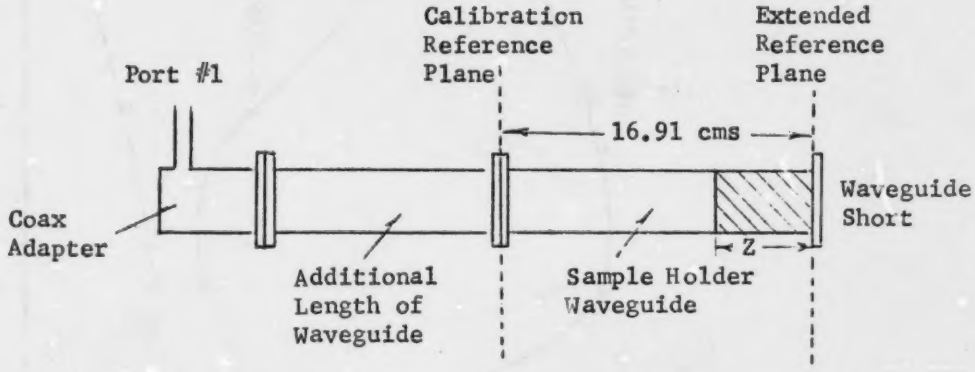


Figure 5. Experimental set up for dielectric property measurements.

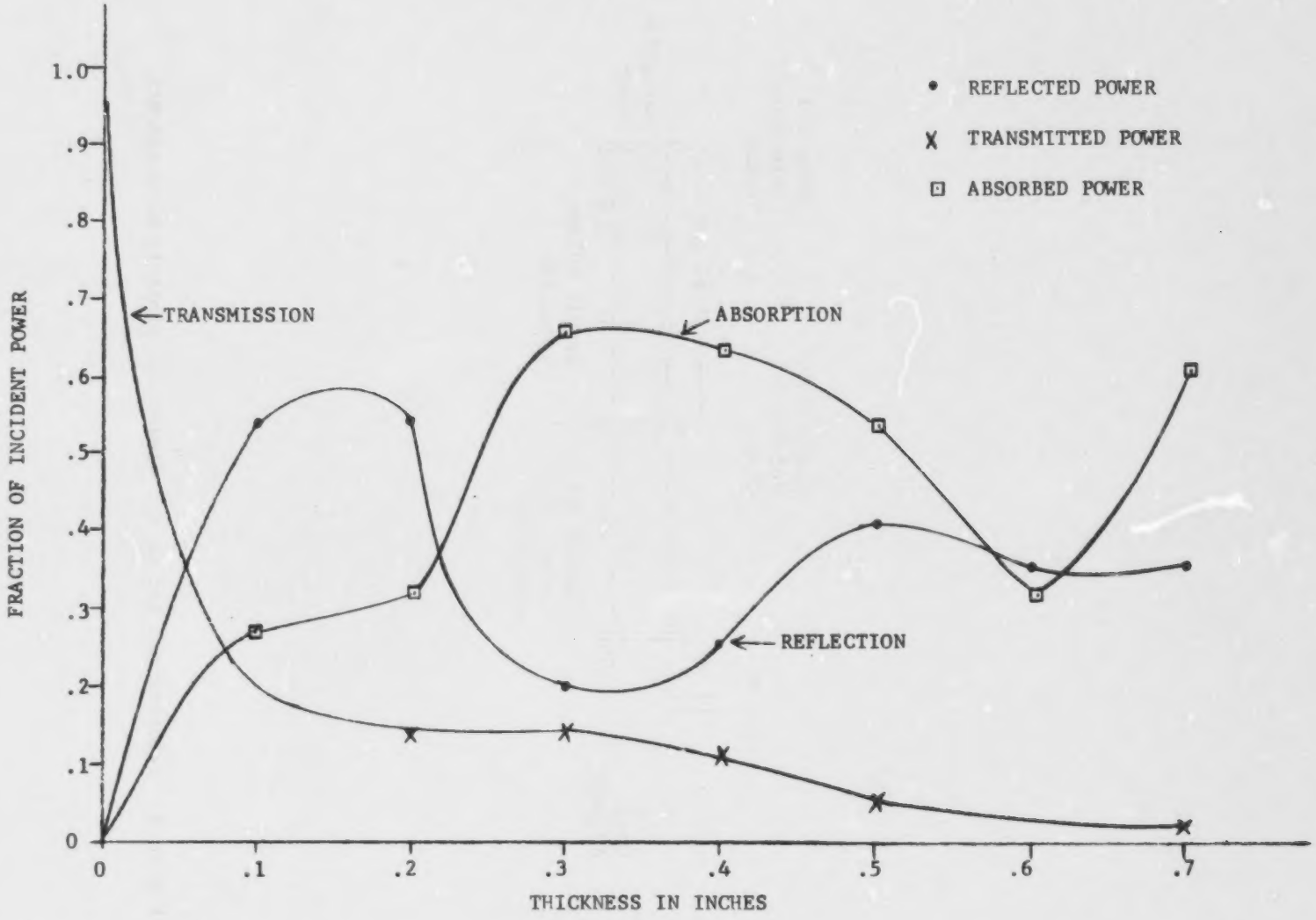


Figure 6. Microwave transmission measurements - Ky. #11 Coal (59%), NaOH (9.4%), H_2O (31.6%).

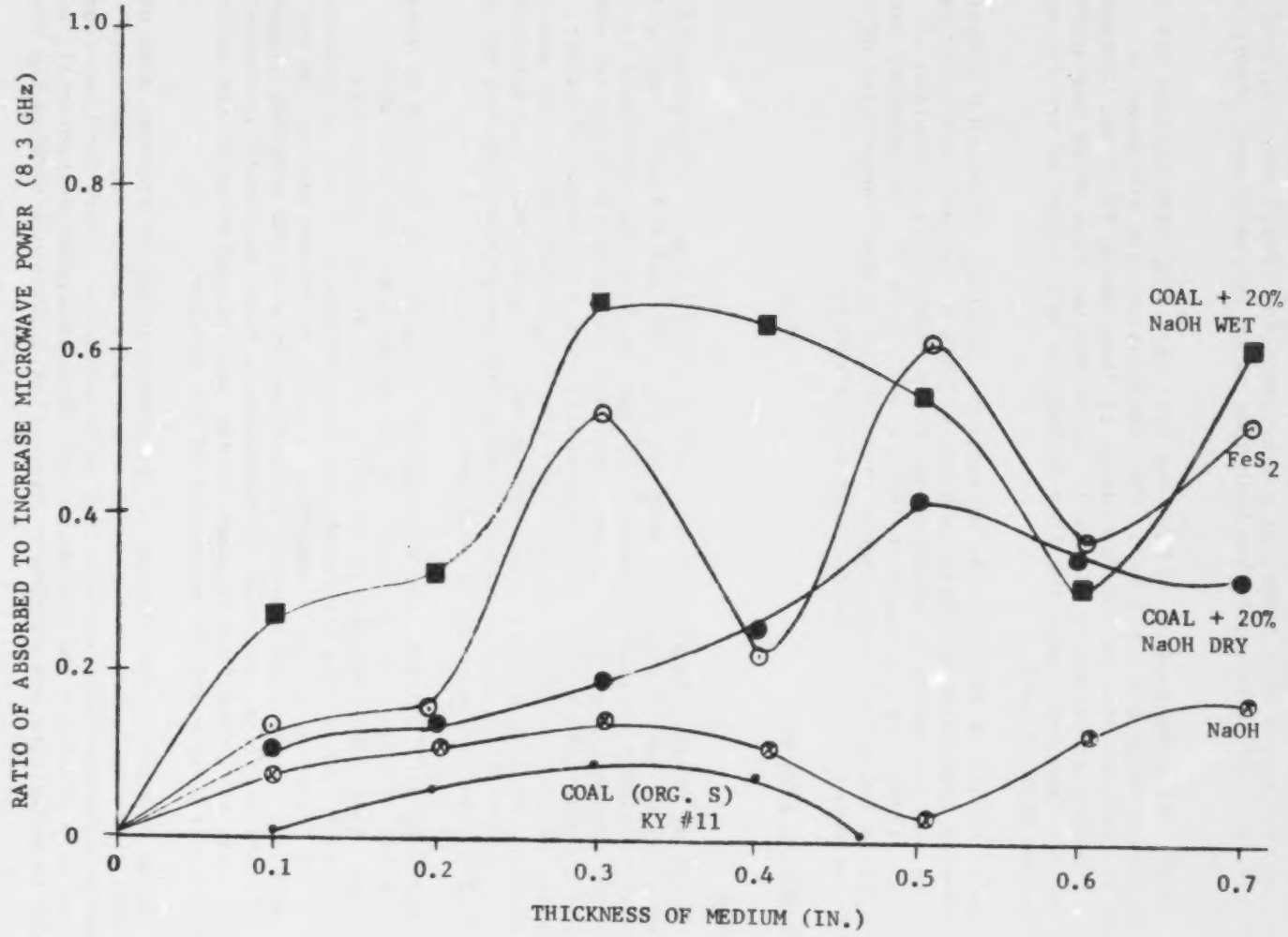


Figure 7. Microwave power absorption.

These measurements show that: a) dry coal free of mineral matter as well as dibenzothiaphene ($C_{12}H_8S_2$) and thianthrene ($C_{12}H_8S$) are essentially transparent to microwaves at 8.3 GHz, b) pyrite particles (FeS_2) are relatively good absorbers and c) moist sodium hydroxide is an extremely good absorbing medium.

Additional measurements on FeS_2 and Coal (Ky. #11) were carried out in the frequency range 0.6 - 4.2 GHz. The transmission data are shown in Figure 8. Reduced data on the dependence of loss factor (ϵ'') vs. frequency (0.6 - 8.3 GHz) are shown in Figure 9. It is obvious from these measurements that in this frequency range the loss in FeS_2 is by a factor of ten (or more) higher than that of coal.

In an effort to identify the behavior of coal/FeS_2 or coal/H_2O mixtures, coal samples containing different amounts of FeS_2 or H_2O were placed in the waveguide and the amount of absorbed power was measured as a function of additive. These data are shown in Table 2 and Figure 10. As expected from the previous individual measurements the addition of small quantities of FeS_2 or H_2O increases the lossiness of coal significantly.

EXPERIMENTAL APPROACH

General

Existing GE-RESD facilities were used in this project. These facilities included: a) microwave sources 2.4 GHz (1 KW, 6 KW) and 8.3 GHz (1 KW) with a specially designed treatment chamber, b) gas handling and analytical instrumentation consisting of several mass spectrometers (time-of-flight and other) and gas chromatographs adequately equipped to handle compounds of sulfur, nitrogen, hydrocarbons, H_2, CO, and H_2O, and c) equipment for sulfur analysis (in coal) as well as a combustion calorimeter for calorific value determinations. In addition, the treatment chamber was instrumented so that net power absorbed by the sample could be measured.

The data obtained from the experiments included: a) accurate measurements of the microwave energy input, b) the gaseous species generated, c) extent of desulfurization, d) calorific value of the treated coal, e) total mass loss during treatment, and f) measurement of surface temperature with an IR pyrometer and bulk temperature using a thermocouple at the end of the exposure. These measurements, in combination with the complete proximate and ultimate analyses, provided by Pennsylvania State University, resulted in a great deal of information relevant to the removal mechanism of the pollutant-forming constituents and the economics of the process.

As an adjunct to the studies of the chemistry of the process, some of the coal types evaluated in the project were subjected to pre- and post-exposure microstructural and electron probe analyses. These data were used to: a) help elucidate the microwave coal desulfurization mechanism(s), and b) aid in explaining any microwave interaction differences between the coals.

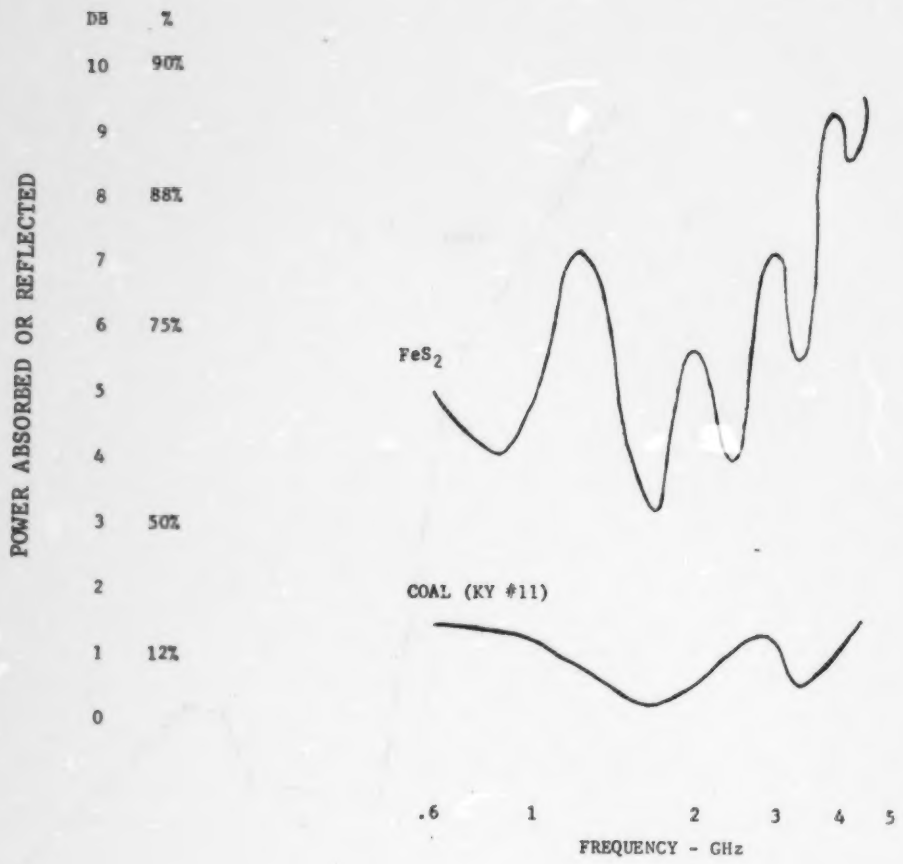


Figure 8. Transmissions coefficient vs. frequency.

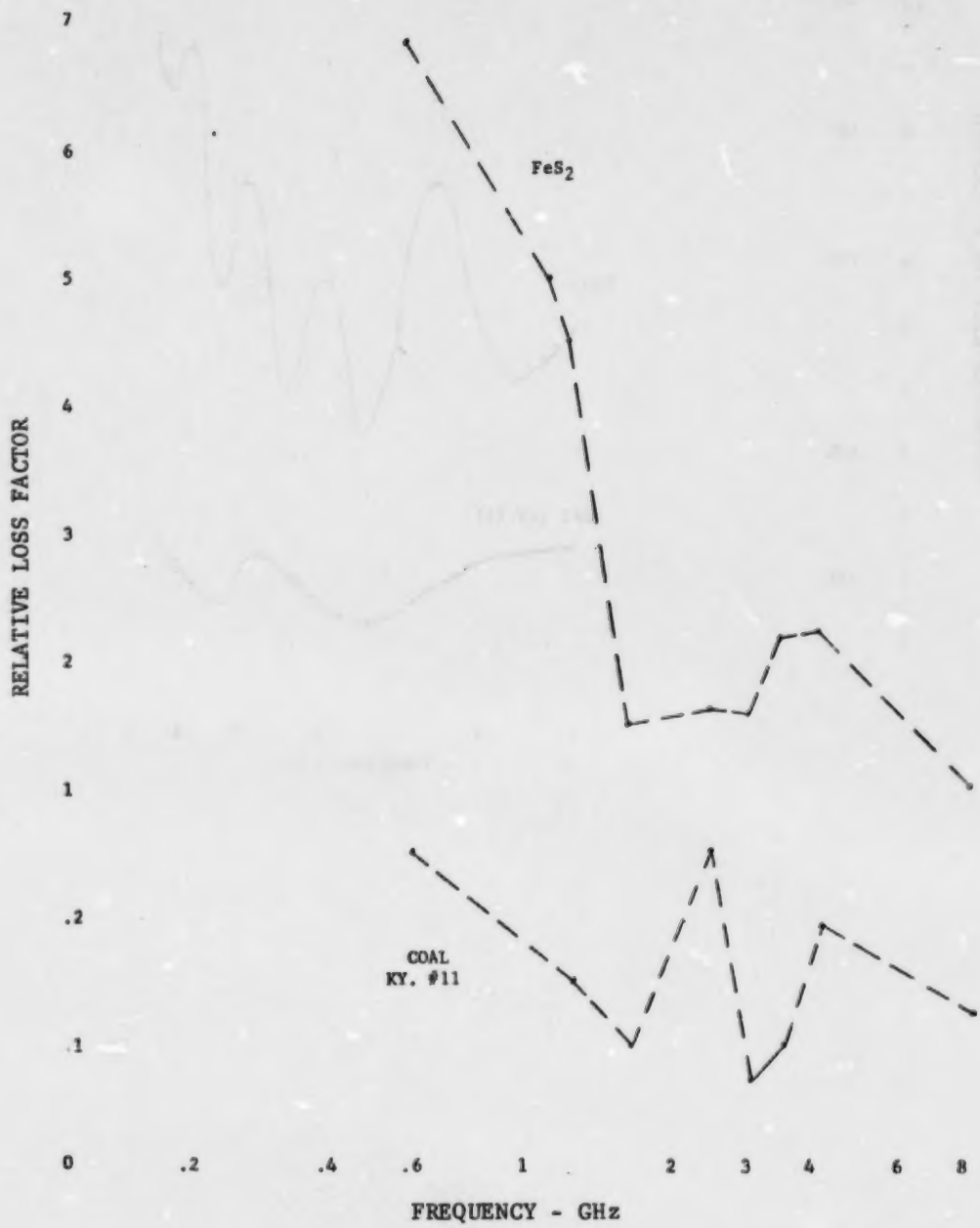


Figure 9. Loss factor variation.

TABLE 2. MICROWAVE POWER ABSORPTION BY KY. #11 COAL IN WAVEGUIDE

Sample	Reduction (db)	% Loss
(Dry) Coal	3	50
Coal + 6.3% Water	7	60
Coal + 14% Water	27	99
Coal + 25% Water	>30	>99
(Dry) Coal + 1% FeS_2	4.5	64
Coal + 3% FeS_2	5	68
Coal + 5% FeS_2	5	79
Coal + 7% FeS_2	5.4	71
Coal + 11% FeS_2	7	80

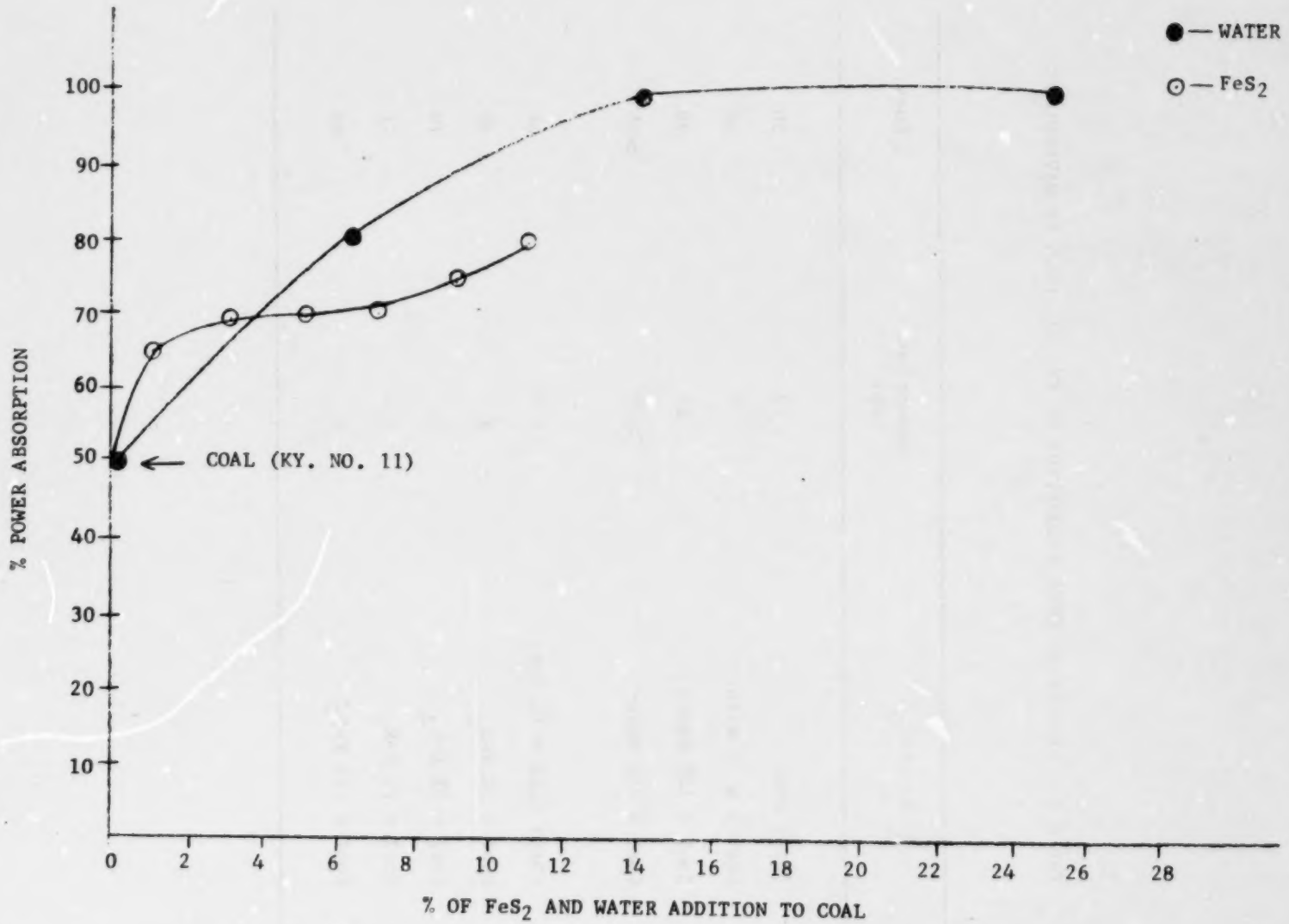


Figure 10. Microwave power absorption by coal in waveguide (at 8.3 GHz).

Microwave Facilities

Coal desulfurization experiments have been carried out with several microwave energy sources. The first was a 1 KW, 8.35 GHz Klystron powered unit assembled at GE, the second was a 2 KW, 2.45 GHz magnetron unit and the third a 6 KW, 2.45 GHz magnetron powered generator. Both 2.45 GHz generators were manufactured by Cober Electronics Inc., Stanford, Connecticut. All three are CW units with power level variable from zero to the rated power. In addition, the units are equipped with dial meter readouts of forward and reflected power. The 6 KW generator has a chart recorder output as well as meter recording.

Figure 11 shows a diagram of the experimental set up used with the 8.35 GHz and the 2.5 KW, 2.45 GHz power sources. Microwave energy is transmitted from the generator via rectangular metal waveguide to an aluminum box applicator (26.7 cm cube). The applicator has a removable lid with a sighting tube and an extension tube which is used as a vent and gas sampling port. The sighting tube has a 15 mm diameter quartz window. Coal powder samples (10-30 g) to be irradiated were placed in a quartz cup (4.5 cm dia. x 7 cm) held by a foam quartz pedestal as shown in the diagram. Air was removed from the applicator using a nitrogen or argon purge. All experiments were run at 1 atmosphere. Figure 12 is a photograph of the 8.35 GHz system which shows the Klystron, the forward and reflected power meters and the applicator box. A photograph of the applicator and box are shown in Figures 13 and 14. Absorption traces at the top of these figures are read to determine the frequency of greatest absorption. The cavity can be tuned for absorption at 8.3 GHz with the coal sample only.

This system is now upgraded with two 6 KW, 2.45 GHz units. The applicator designed for use with the two 6 KW generator is a steel pressure vessel 45.7 cm dia. x 914 cm length. This unit will provide a facility in which kilogram quantities of coal samples can be irradiated. A turntable was designed and constructed to enable rotation of the containerized coal samples during irradiation in the applicator. This ensures more uniform exposure to the microwave field. A diagram of the turntable is shown in Figure 15. The table is a foam quartz disc 21 cm dia. x 2.5 cm which has a pyrex test tube mounted on the under side as shown in the diagram. The disc rotates on a pointed teflon rod attached to a foam quartz base. The turntable is rotated by directing a stream of N_2 against grooves cut radially into the under side. With moderate flows 2-3 rps are produced. Samples to be irradiated are held in a pyrex petri dish 14 cm dia. x 1.5 deep or in pyrex beakers. This arrangement has been used to treat samples up to 500 g.

Analytical Procedures

One of the sulfur analysis techniques used was adopted from ASTM Procedure E30 "Sulfur by Direct Combustion - Iodate Titration Method." A known weight of sample of coal to be analyzed is placed in a combustion boat and ignited in a stream of oxygen at temperatures in excess of 1100°C. The SO_2 produced is absorbed in an acidified starch-iodide solution and determined during the combustion, by titration with a potassium iodate solution. The following reactions are involved in the process:

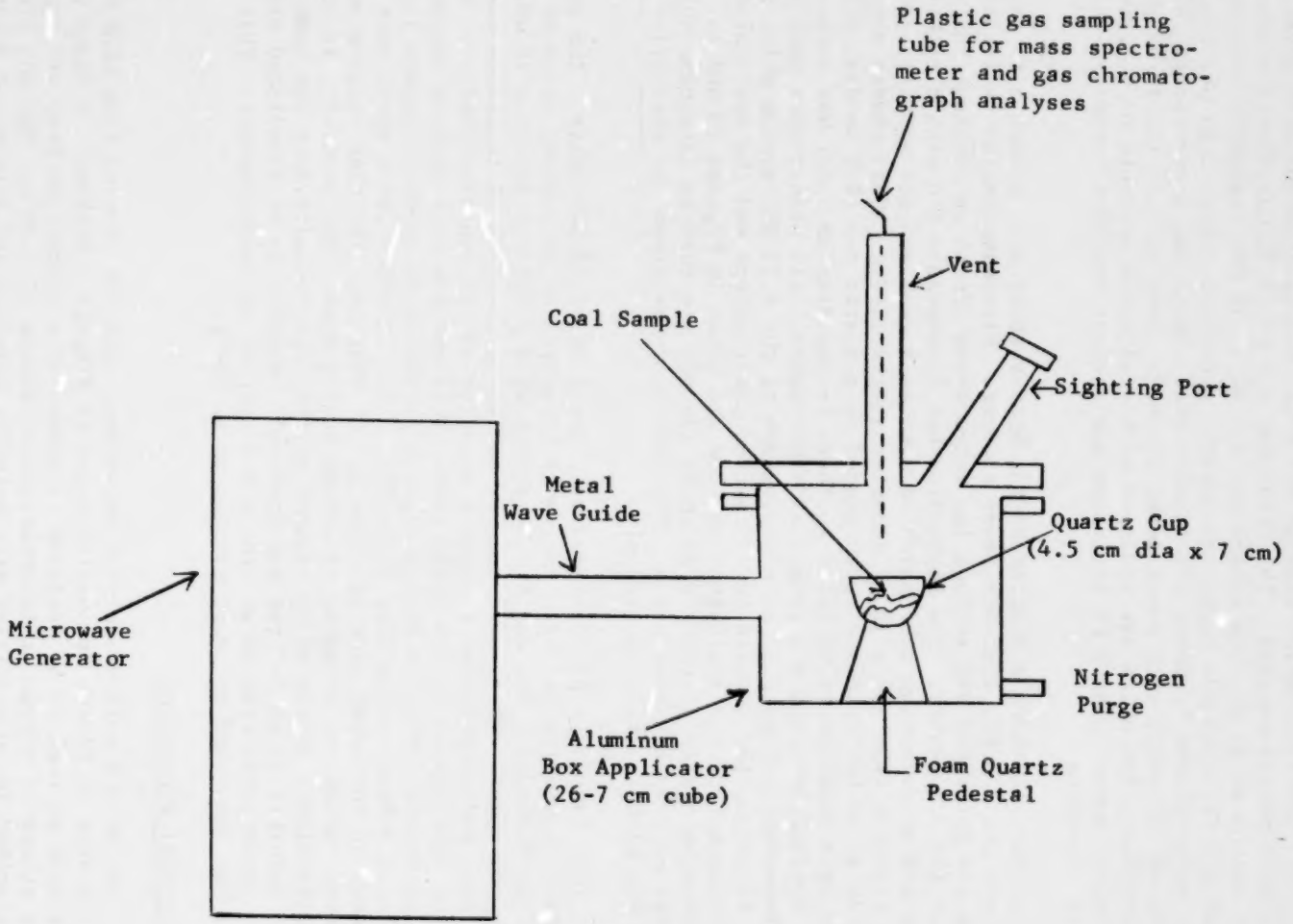

Plastic gas sampling tube for mass spectrometer and gas chromatograph analyses
Vent
Coal Sample
Sighting Port
Metal Wave Guide
Quartz Cup (4.5 cm dia x 7 cm)
Microwave Generator
Nitrogen Purge
Aluminum Box Applicator (26-7 cm cube)
Foam Quartz Pedestal

Figure 11. Diagram of microwave desulfurization apparatus, 8.35 GHz and 2.45 GHz experiments.

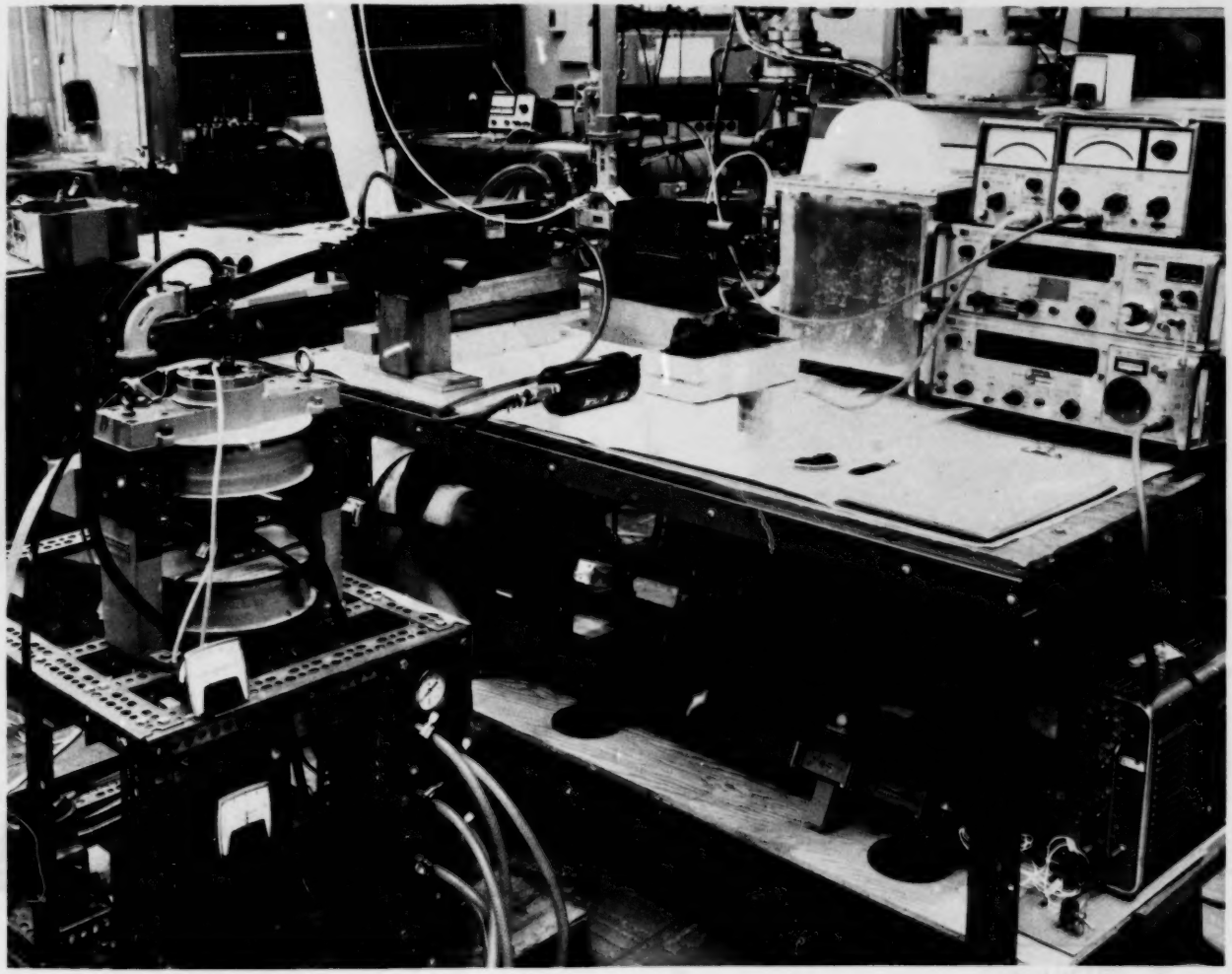
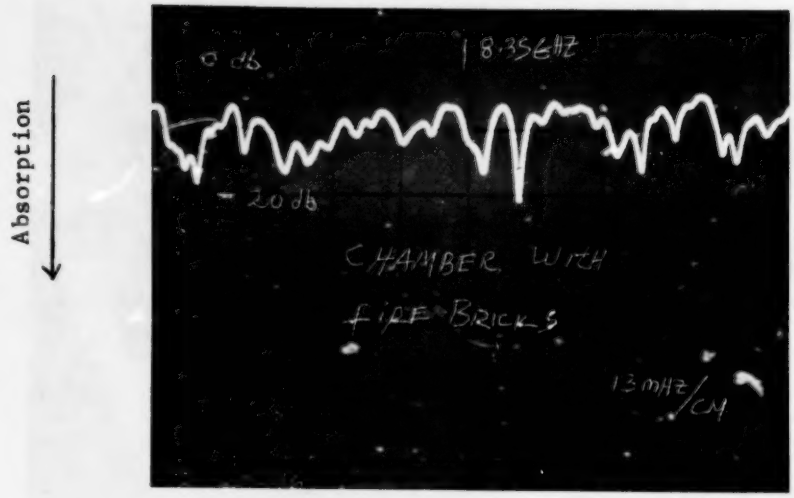


Figure 12. 8.35 GHz microwave equipment and measurement apparatus.



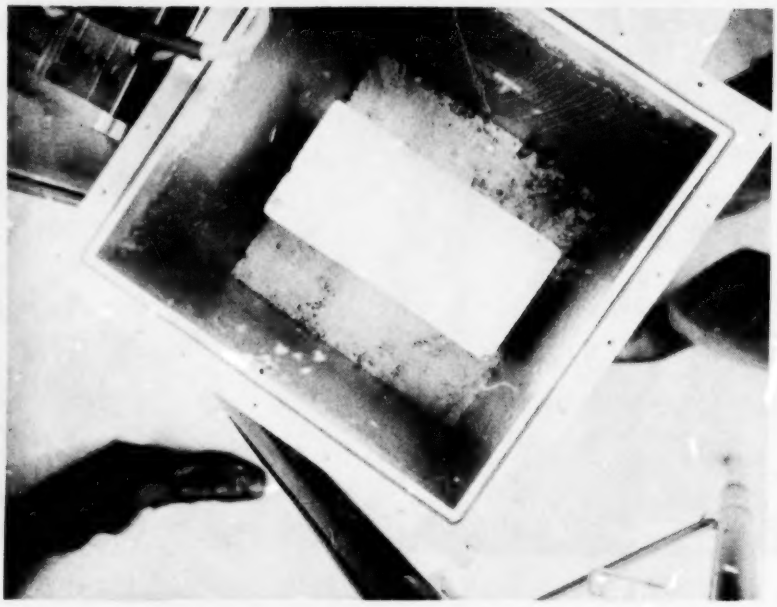
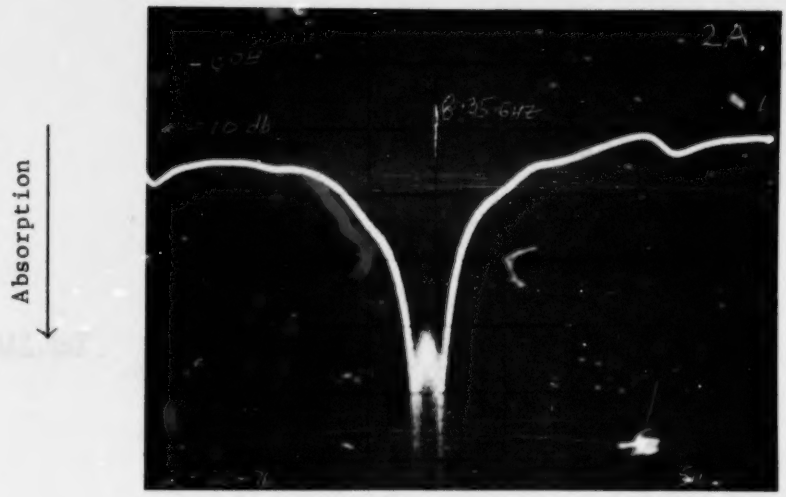


Figure 13. Treatment chamber and sample holder.



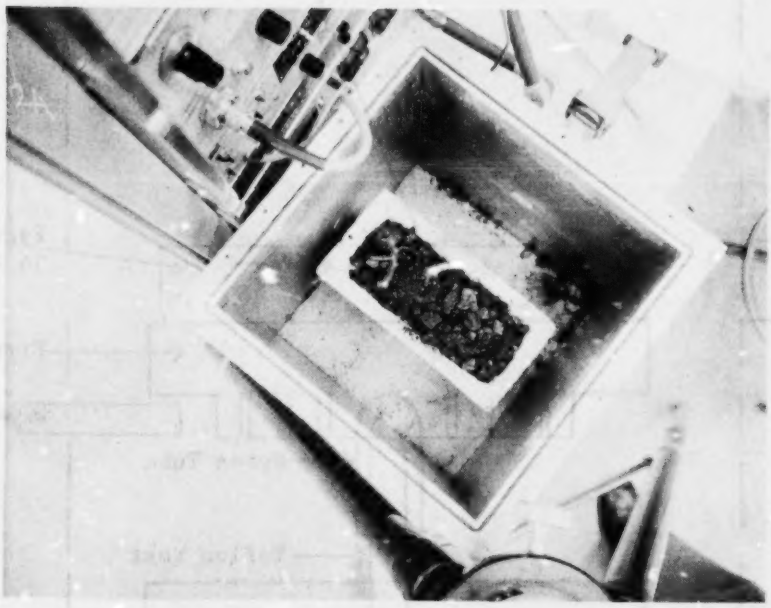


Figure 14. Treatment chamber with coal sample (500g).

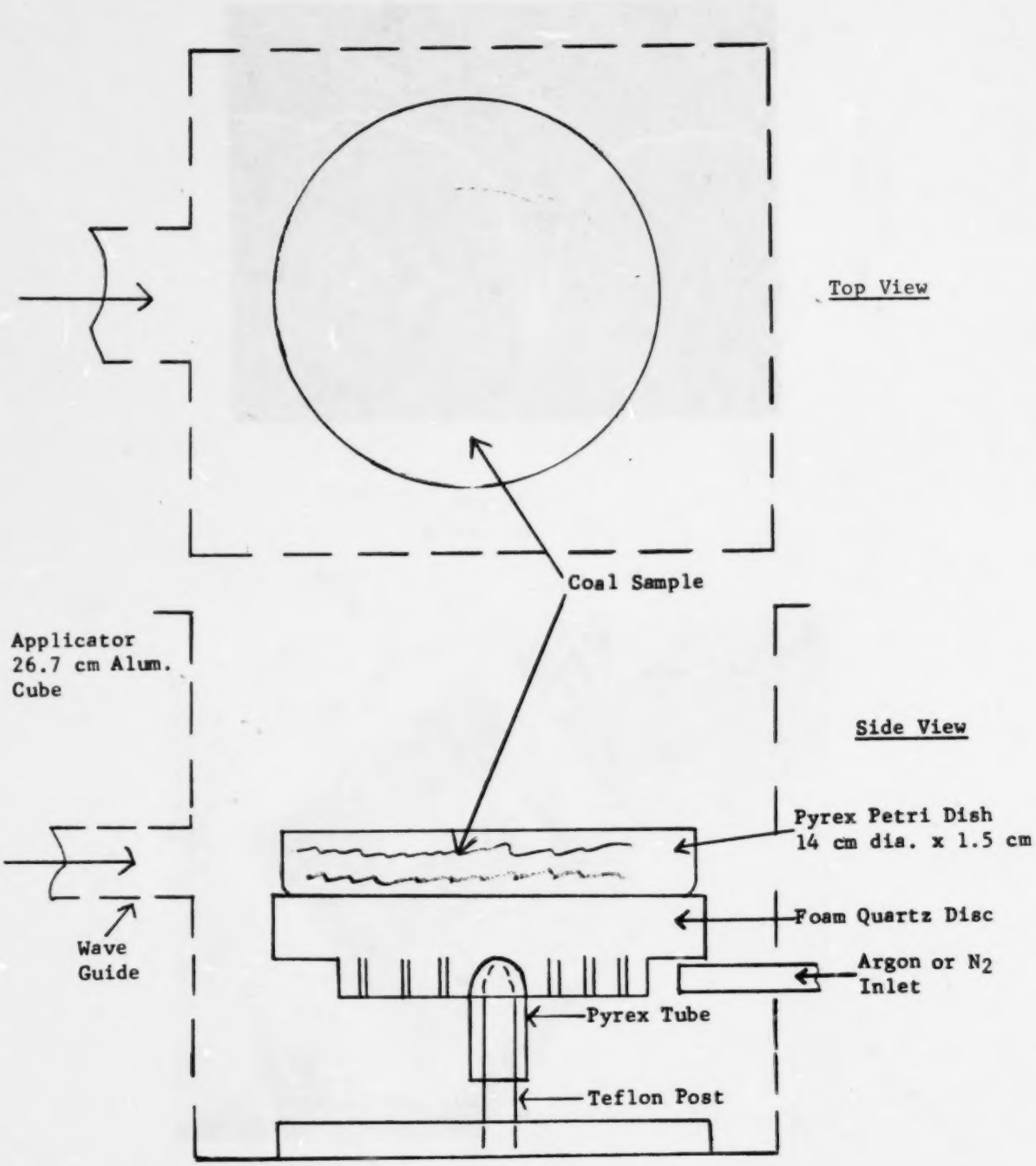


Figure 15. Diagram of turntable used in 6 KW 2.45 GHz experiments.

$$KIO_3 + 5\ KI + 6\ HCI = 3\ I_2 + 6\ KCI + 3\ H_2O$$

$$SO_2 + I_2 + 2\ H_2O = H_2\ SO_4 + 2\ HI$$

where the liberated I_2, in an aqueous solution, is oxidized by SO_2 to HI.

This procedure determines only combustible sulfur, which ends up as SO_2. Sulfur tied up in the ash is not determined by this technique.

Other analytical techniques used in this work involved use of the LECO (IR-33) Sulfur Determinator which burns the sample at a temperature as high as 1600°C and analyzes for SO_2 using an infrared detector. This technique has been shown to detect all sulfur present.

Comparison of results obtained by the above techniques with total sulfur determinations based on the Eschka method showed good agreement on untreated samples. In the case of treated samples the Eschka method in some cases detected sulfur levels one to three tenths of a percent higher than the lower temperature combustion method thus suggesting some capturing of sulfur in the ash.

Mott's method was used for the determination of sulphate and pyritic sulfur whenever these analyses were deemed necessary. The method is based on acid extractions of two samples of pulverized coal. One sample is extracted with hydrochloric acid, the other with nitric acid and the amount of iron is determined in the extracts. Values thus determined are used to calculate the pyritic sulfur content of the coal. Organic sulfur cannot be measured directly and is calculated from the relationship

$$\%\ S_{organic} = S_{total} - (S_{pyritic} + S_{sulphate})$$

Determinations of C, H, and N were made with a Perkin Elmer Elemental Analyzer - Model 240. This is an instrument which accurately determines the C, H, and N content of organic compounds by detecting and measuring their combustion products (CO_2, H_2O and N_2). The combustion is carried out in pure oxygen under static conditions with the combustion products being analyzed automatically in a self integrating steady-state, thermal conductivity analyzer.

Ash content is determined from the residue of either the lower temperature combustible sulfur analysis or the C, H, and N analysis.

There is no simple direct method for the determination of oxygen. Oxygen was calculated from the relationship

$$\%\ O = 100 - (\%\ N + \%\ C + \%\ H + \%\ S + \%\ Ash)$$

The proximate analysis of coal consisting of moisture loss, % ash, % volatiles and % fixed carbon was determined by a thermogravimetric procedure developed and recommended by the Perkin Elmer Corporation. In this analysis the sample is weighed directly into the instrument at room temperature under a N_2 purge. The temperature is then raised to 100°C and the N_2 flow rate

increased. At the end of five minutes (sufficient time to dry the sample) the N_2 flow rate is reduced to the initial level and the sample is reweighed. The difference between the initial and the second weight represents the loss in weight due to moisture. The temperature of the sample is then rapidly raised to 950°C, while maintaining a constant N_2 flow, and is held 5 to 10 minutes. The total weight loss for the sample minus that for moisture loss is due to volatiles; the % fixed carbon is calculated from the relationship

$$\% \text{ C} = 100 - (\% \text{ Volatiles} + \% \text{ Ash})$$

The results obtained by the above technique agree quite well with the results obtained using the A.S.T.M. procedure D271 - 64. A typical plot of weight versus time-temperature is shown in Figure 16.

Microstructural Characterization

A series of coal samples were examined before and after exposure to microwaves using standard scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) techniques. This provided information as to the effects of treatment on surface topography and the level and spatial distribution of sulfur as well as other contaminants such as Al, Si, Cu, K and Fe.

Energy dispersive x-ray techniques greatly enhance the analytical value of the SEM as the characteristic x-rays emitted under bombardment by electrons provide both qualitative and quantitative information about the nature and amount of elements present in the volume excited by the primary electron beam. For this study, the scanning electron microscope was equipped with a non-dispersive spectrometer. With this type of equipment, the energy of the x-ray photons generated is converted into an electrical pulse in a silicon crystal. A bias voltage applied to the crystal collects the charge, which is proportional to the energy of the x-rays. The pulse is amplified, converted to a voltage pulse and fed into a multichannel analyzer. The resulting spectrum for elements above fluorine (atomic number 9) is subsequently plotted on a chart after a sufficient period of counting to insure adequate accuracy. Data plotting was carried out at two levels of sensitivity, namely, 10^4 and 5×10^4 counts for full scale chart deflection. In addition, SEM interfaced rays can be photographically recorded for the various impurities present.

SEM/EDX studies were conducted on two types of samples. In one set, the coal particles, approximately 1/8 inch in diameter, were cleaved and the cleaved surfaces examined for topography and sulfur distribution by SEM interfaced mapping. In the other techniques, 100 mesh coal particles were pressed into a small cavity in standard spectroscopically pure carbon SEM mounts and the small powder compacts subsequently carbon shadowed to provide appropriate electrical characteristics. EDX studies on the carbon mount and carbon shadowing material indicated that they were quite pure and did not have any significant effect on the apparent compositional characteristics of the coal samples.

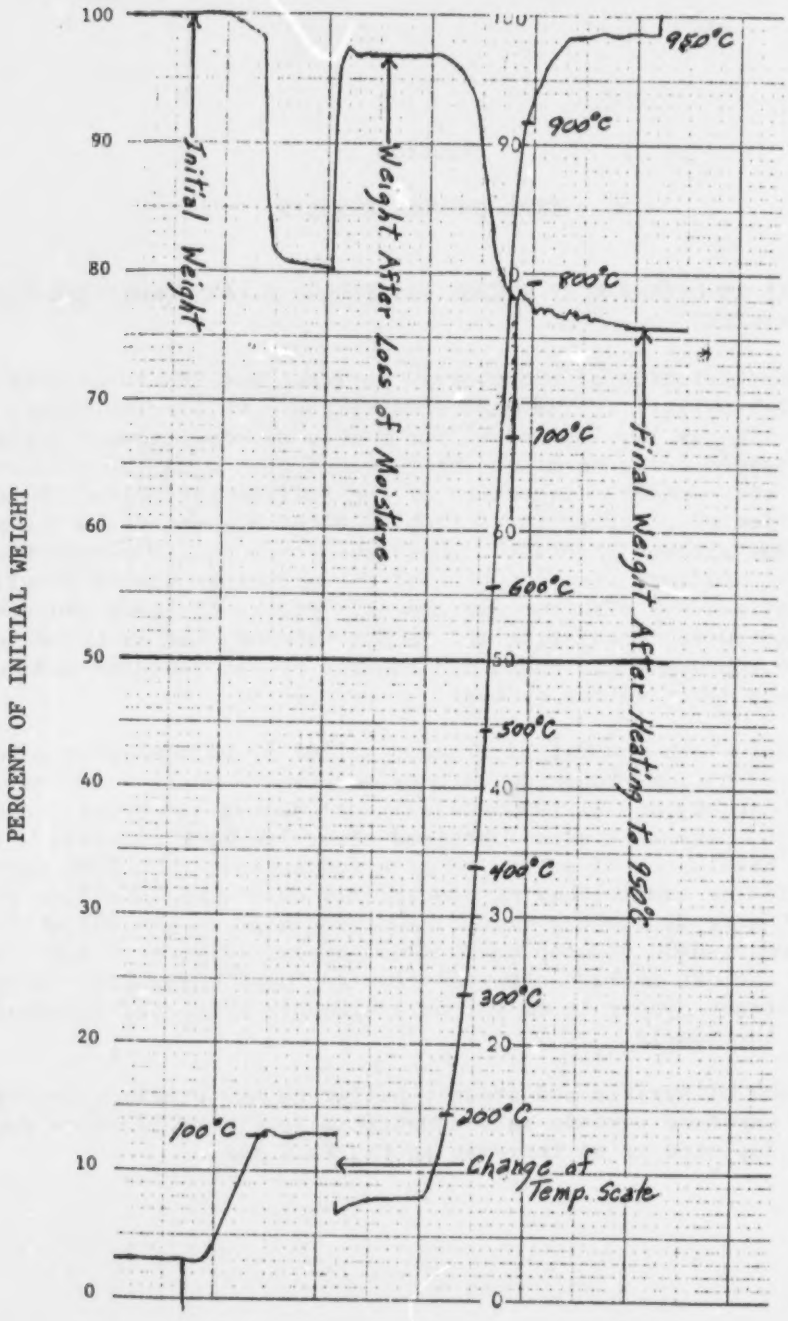


Figure 16. Temperature dependence of weight change for coal.

SECTION 4

EXPERIMENTAL RESULTS

SULFUR REMOVAL AS OBSERVED BY ENERGY DISPERSIVE X-RAYS (EDX) AND ELECTRON PROBE MICROANALYSIS

The characteristics of the cleaved surfaces and SEM interfaced EDX sulfur maps for a high pyritic sulfur coal (Pennsylvania #6 Clarion County with ~4% S) are shown in Figures 17, 18, and 19 for 3 sets of conditions. Figure 17 shows the smooth cleaved surfaces of the as-received coal with the sulfur map* indicating a very uniform dispersion of the sulfide particles. Figure 18 is a similar series of pictures for a sample heated 90 seconds in the microwave unit (8.35 GHz) without leachant. These results indicate a reduction in sulfur content and some fragmentation of the structure due to coupling of the FeS_2 particles and H_2O with the microwaves. Figure 19 shows the combined effects of microwave irradiation and NaOH treatment. It is to be noted that the structure appears to be uniformly altered by the leachant and has an apparently much lower sulfur content.

Evidence for the removal of organic sulfur by microwave irradiation in the presence of sodium hydroxide is provided by the energy dispersive x-ray spectra for Kentucky No. 11 (PSOC-273-1) coal before and after treatment and the residue from the wash water obtained after leachant removal. Figure 20 shows a very high ratio of sulfur to iron and supports the Penn State analysis of this particular sample showing essentially only organic sulfur (4.8%) (Table 3). Figure 21 shows a significant reduction in the sulfur peak height for the microwave/NaOH treated and washed sample. Figure 22 displays the spectrum for the dry residue obtained from the wash water after evaporation; sulfur and silicon appear to be the only elements extracted in significant amounts from the sample.

The attack of pyritic and organic sulfur on the previous two samples during short exposure periods is demonstrated in Figure 23 where the reduction in sulfur is depicted as an increase in the Fe/S ratio.

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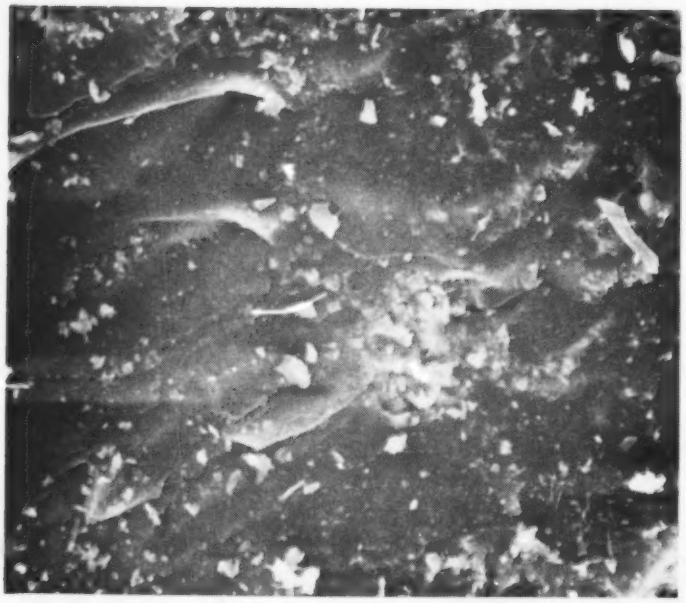
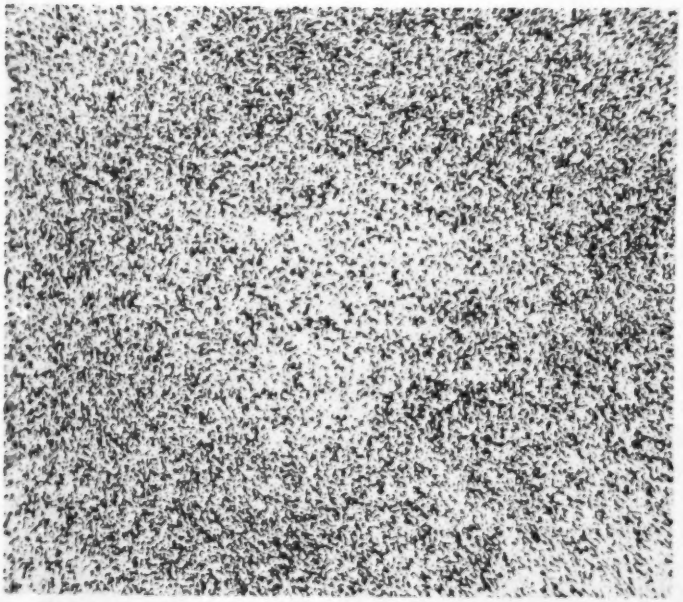
* In a sulfur map obtained by the EDX microanalytical technique, the density of white dots at any location is a direct function of sulfur content whether present as sulfide particles or organic compounds.

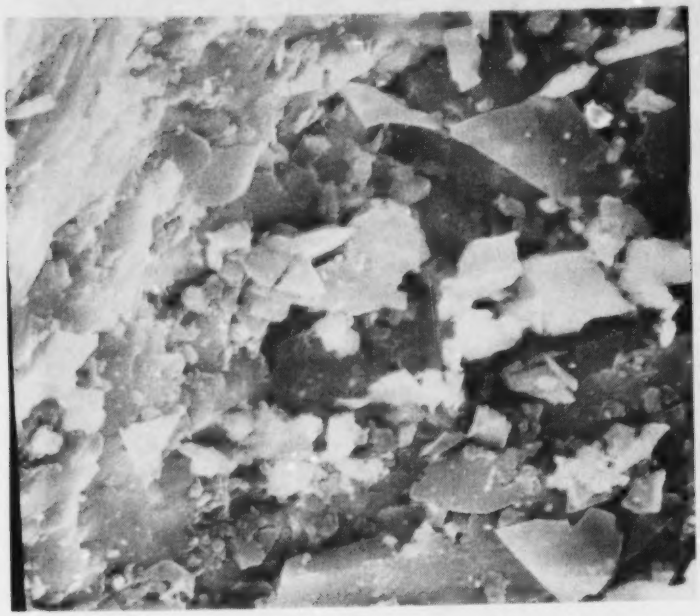


(a)



(b)

Figure 17. (a) Scanning electron micrograph and (b) SEM interfaced sulfur map for a cleaved surface of virgin #6 Pennsylvania coal (pyritic), 300X.

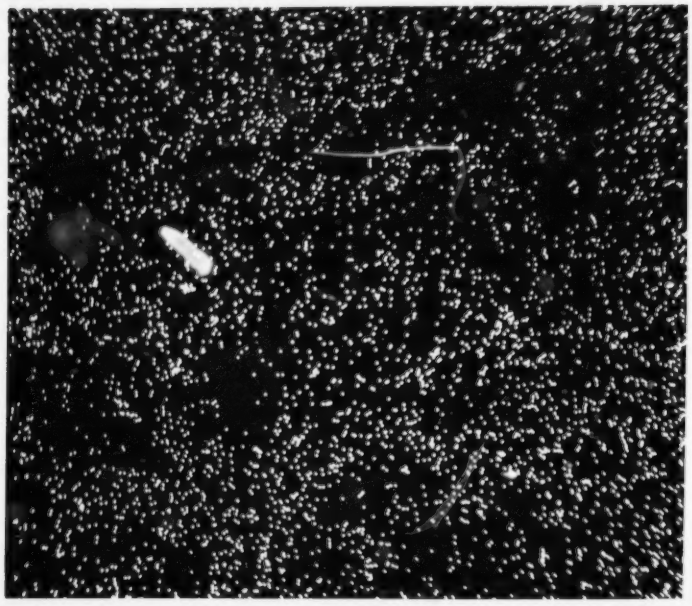


(a)

(b)

Figure 18. (a) Scanning electron micrograph and (b) SEM interfaced sulfur map for a cleaved surface of #6 Pennsylvania coal heated 90 seconds with microwaves, 300X.

(a)



(b)

Figure 19. (a) Scanning electron micrograph and (b) SEM interfaced sulfur map for a cleaved surface of #6 Pennsylvania coal heated 90 seconds with microwaves in presence of NaOH, 300X.

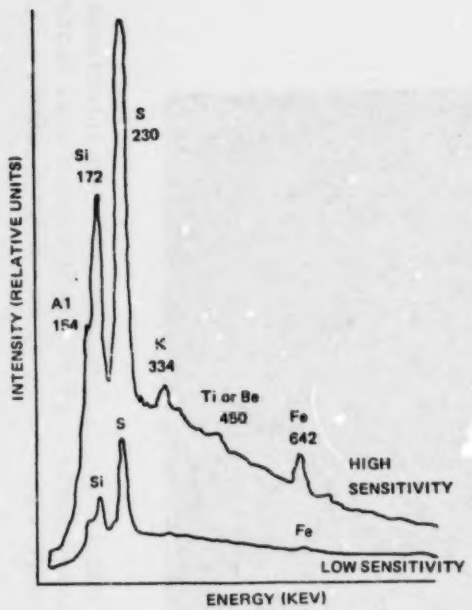


Figure 20. Energy dispersive x-ray spectrum for virgin sample PSOC-273-1 (Ky. #11)

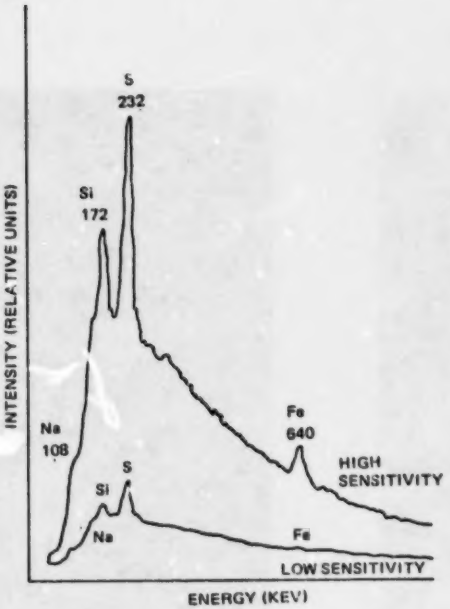


Figure 21. Energy dispersive x-ray spectrum for PSOC-273-1 coal after 30 second microwave exposure using NaOH leachant (sample washed).

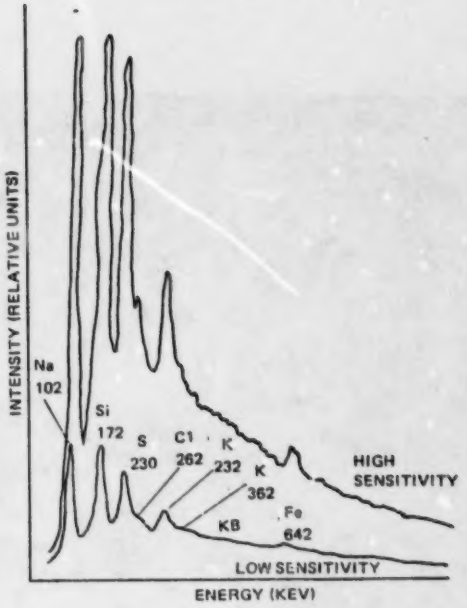


Figure 22. Energy dispersive x-ray spectrum for residue from wash water from leachant/microwave irradiation treated PSOC-273-1 coal.

TABLE 3. CANDIDATE COAL SAMPLES

Coal #	Geographic Origin	Sulfur Content, %			
		Pyritic	Organic	Sulfatic	Total
PSOC-320	Pittsburgh Seam, Berlin, Pa.	0.45	0.64	0.07	1.16
PSOC-257	Upper Freeport Seam from Pa.	1.06	0.56	----	1.62
PSOC-294	Pittsburgh Seam from Pa.	2.27	0.34	0.01	2.62
PSOC-255	Lower Kittanning Seam from Pa.	4.49	0.78	0.03	5.30
PSOC-353	Clarion Seam from Pa.	4.65	1.21	0.07	5.93
Pa. #5	Upper Kittanning Seam, Clarion County, Pa.	2.37	0.2	----	2.57
Pa. #6	Upper Freeport Seam, Clarion County, Pa.	3.8	0.2	----	4.0
PSOC-273-1	Ky. #11 Seam, Sinclair Strip Mine	0.18	5.71	0.02	5.91
PSOC-273-2	Ky. #11 Seam	2.63	1.87	0.14	4.64
PSOC-270	American Seam, Maxine Mine, Al.	0.02	2.70	0.05	2.77

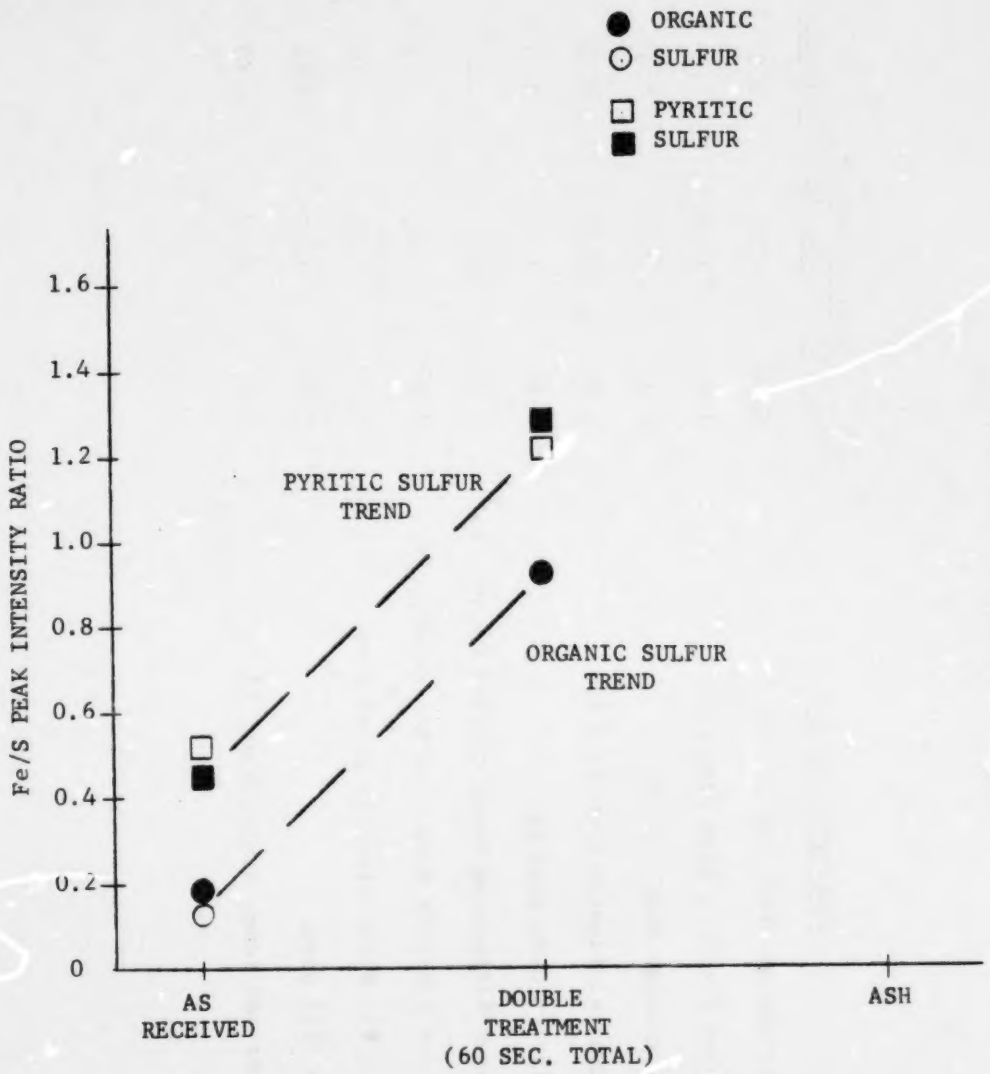


Figure 23. Iron to sulfur ratio by dispersive x-rays.

In addition to the EDX measurements, electron probe x-ray microanalysis (wavelength dispersive spectroscopy) was used to look at high pyritic coal samples from L. Kittanning (PSOC-255, Table 3). Measurements of Fe-Kα and S-Kα X-radiation (at respective wavelengths of 1.9373Å and 5.372Å) were made on the as-received sample and a sample (¼" particle size) which was exposed to a microwave field of 2.45 GHz for sixty seconds under argon in the absence of sodium hydroxide. The counts recorded over a 100 second period for Fe and S are shown in Table 4 for the treated sample as well as for as-received material and an FeS standard. These measurements show that the sulfur in the untreated sample exists primarily as FeS_2 while in the treated (at least in the areas under investigation) the ratio of S/Fe has been significantly reduced below that corresponding to FeS, thus suggesting the possibility of converting some of the pyritic sulfur to organic forms.

COAL DESULFURIZATION AS EVIDENCED BY SULFUR CHEMICAL ANALYSIS

General and Temperature Measurements

Initial experiments using microwave irradiation of coal (without leachants) at 8.3 GHz involved samples either high in pyritic or high in organic sulfur. Those early measurements (26) showed that significant amounts of pyritic sulfur can be removed (~50%) in exposure times of less than one minute with the generation of H_2S (and much smaller amounts of COS and SO_2 identified by mass spectrometry). The accompanied mass losses were essentially limited to sulfur and water removal. Coal samples with high levels of organic sulfur however failed to show any reduction of the organic sulfur level at this frequency. These results were explained mainly in terms of reactions between FeS_2 and bound hydrogen releasing H_2S.

In an effort to address the total sulfur problem (pyritic and organic) sodium hydroxide was brought into the picture since it is favored thermodynamically to react with pyritic sulfur and has been found (empirically by the petroleum industry) to dissolve or react with organic sulfur compounds. The sodium hydroxide is added as a water solution which produces a slurry with the coal which, in turn, is partially dried before it is exposed to the microwave field. All the work to date has been accomplished at frequencies of 0.22, 2.45 and 8.3 GHz. Typical exposure times range up to 60 seconds, and the observed bulk temperature is less than 300°C. After exposure, the sample is washed in water and the coal is analyzed for total sulfur using techniques such as the Leco or the Eschka methods.

Since the temperature and heating time control the extent of volatilization and loss in calorific value of coal, a considerable amount of care was exercised in monitoring the surface temperature during sample irradiation as well as measuring the bulk temperature. The surface temperature was monitored by looking at the sample with an automatic recording IR pyrometer, Model 300 Ircon, 2-2.5 micron band pass. The bulk sample temperature was determined by inserting a thermocouple into the sample as soon as the microwave power supply was turned off. Typical traces of surface temperature are shown in Figure 24 for Lower Kittanning Coal (PSOC-255) containing 16% sodium hydroxide. Although there were differences of ten to fifty degrees in recorded surface

TABLE 4. ELECTRON PROBE X-RAY MICROANALYSIS OF COAL SAMPLES

Counts for (100 sec.) Fe	Counts for (100 sec.) S	Sample	Fe/S (Ratio)	S/Fe (Ratio)	X (in FeS_x)
73544	182962	As received PSOC-255 (0.25")	0.41	2.44	1.81
72843	190520		0.38	2.63	1.95
15894	1109	PSOC-255 Exposed in M.W.	14.33	0.070	0.052
21657	5317		4.07	0.246	0.182
7865	390		20.17	0.0496	0.037
113893	155364	Strd. FeS	0.73	1.37	1.01
111860	148661		0.75	1.33	0.985

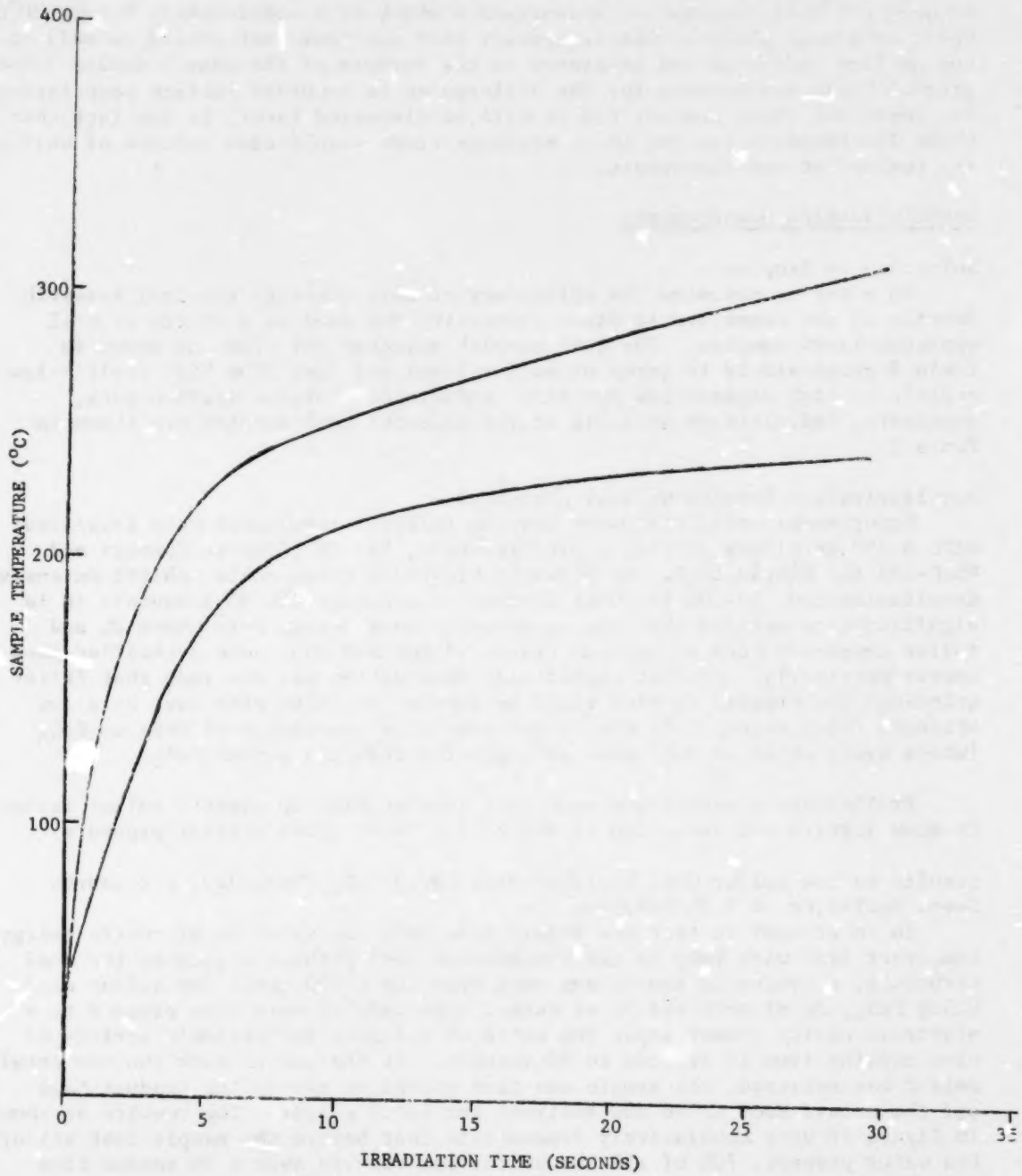


Figure 24. Surface temperature of PSOC-255 (L. Kittanning) coal during microwave exposure in the presence of sodium hydroxide.

temperatures between presumably identical runs there was much closer agreement between the bulk temperature measurements which were consistently below 250°C. Based on visual observations it appears that hot spots and arcing as well as sodium line radiation are generated on the surface of the sample during irradiation. These may account for the differences in recorded surface temperatures. The important thing however (as it will be discussed later) is the fact that at these low temperatures and short exposure times significant amounts of sulfur are removed at one atmosphere.

Desulfurization Measurements

Selection of Samples--

In order to maximize the efficiency of this activity the Coal Research Section of the Pennsylvania State University was used as a source of well characterized* samples. The coal samples selected for study as shown in Table 3 range widely in terms of sulfur level and form from high pyritic-low organic to high organic-low pyritic. Additional characterization data, proximate, and ultimate analysis of the selected coal samples are shown in Table 5.

Desulfurization Results Without Leachants--

Experiments using microwave heating (without leachants) were initiated with 0.25" particles of highly pyritic coals, Pa. #6 (Clarion County) and PSOC-255 (L. Kittanning). As shown in Figure 25 these coals exhibit extensive desulfurization 40-60% in short periods of exposure (20-60 seconds); it is significant to mention that the accompanied mass losses were about 6% and sulfur compounds (such as H_2S and traces of COS and SO_2) were identified mass spectrometrically. Another significant observation was the fact that (after grinding) the treated samples could be further purified with ease by a low strength (bar) magnet (30) due to the extensive conversion of FeS_2 to FeS_x (where $x \leq 1$) which is much more paramagnetic than its parent FeS_2.

Preliminary measurements with coal samples high in organic sulfur failed to show significant reduction in the sulfur level after similar exposure.

Results on Low Sulfur Coal Enriched with Added FeS_2 (PSOC-320, Pittsburgh Seam, Berlin,Pa. + 5.3% FeS_2)--

In an attempt to test the theory that NaOH activated by microwave energy can react fast with FeS_2 in the presence of coal without degrading the coal structure, a synthetic slurry was made from 10g (-100 mesh) low sulfur coal, 0.53g FeS_2, 2g of NaOH and 5g of water. The samples were then exposed to a microwave cavity (power input 300 watts at 8.3 GHz) for variable periods of time ranging from 10 seconds to 90 seconds. At the end of each run the total weight was measured, the sample was then washed to remove the product Na_2S and the excess NaOH dried and analyzed for total sulfur. The results as shown in Figure 26 very conclusively demonstrate that before the sample lost all of the water present, 70% of all the sulfur was removed over a 90 second time period.

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* Characterization was done by Commercial Testing and Engineering, Co., Chicago, Ill.

TABLE 5. S, C, H, N, O, ASH, MOISTURE, VOLATILE MATTER, AND FIXED CARBON OF SAMPLE COALS

Coal	Combustible Sulfur (%)	Nitrogen (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	Ash (%)	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)
Pa. #5	2.37	1.53	78.82	5.69	9.12	2.47			
PSOC-26	3.08	1.72	66.11	4.40	10.77	9.62	4.3	37.8	52.6
PSOC-252	3.65	1.68	66.74	4.92	7.57	11.24	3.0	41.0	47.8
PSOC-255	4.3	.85	62.78	3.91	10.39	17.84			
PSOC-257	1.60	1.40	71.48	5.02	11.00	10.55	0.7	27.19	62.26
PSOC-270	1.95					17.4			
PSOC-272	2.45					5.4			
PSOC-273-1	4.78	1.33	60.19	4.80	18.62	12.88			
PSOC-294	2.45	1.21	62.65	4.24	10.08	19.94	0.7	34.74	45.32
PSOC-296	1.24	2.35	68.23	4.99	8.03				
PSOC-320	1.16						4.0		

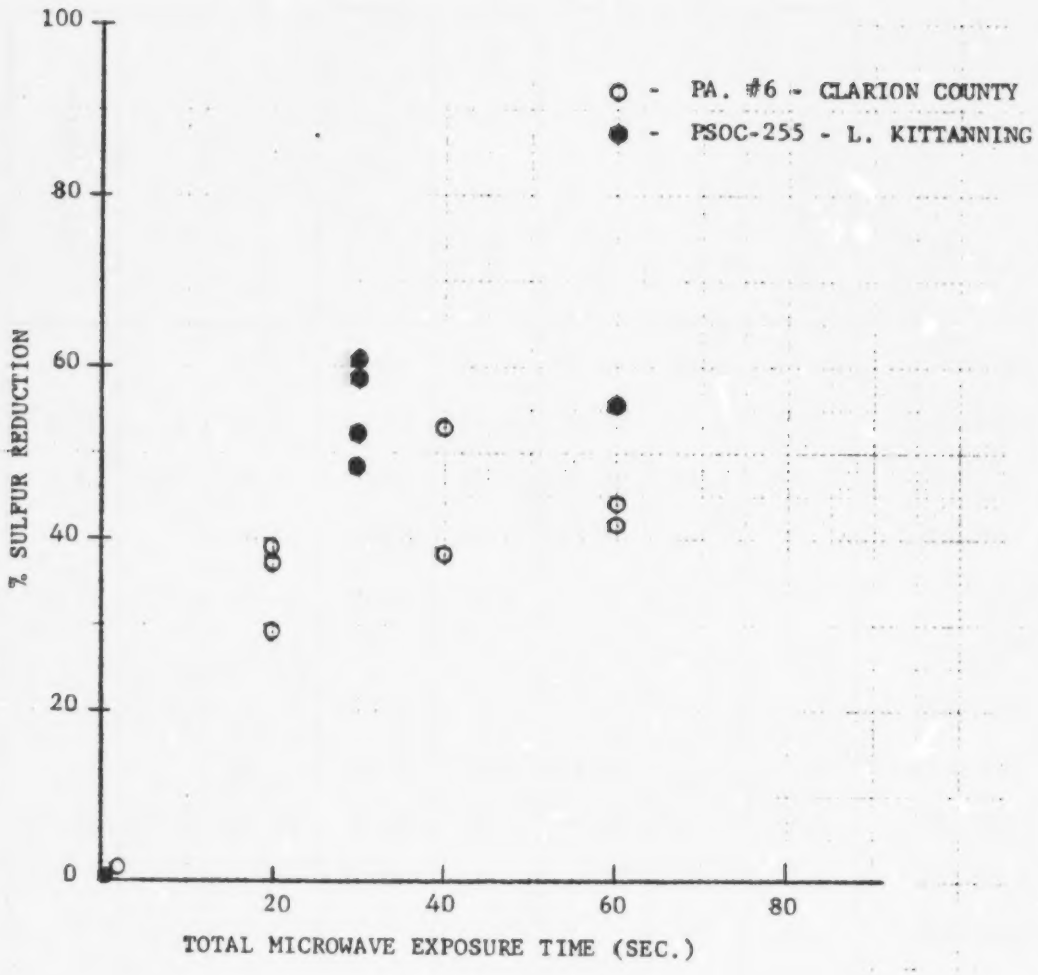

Figure 25. Reduction of total pyritic sulfur.

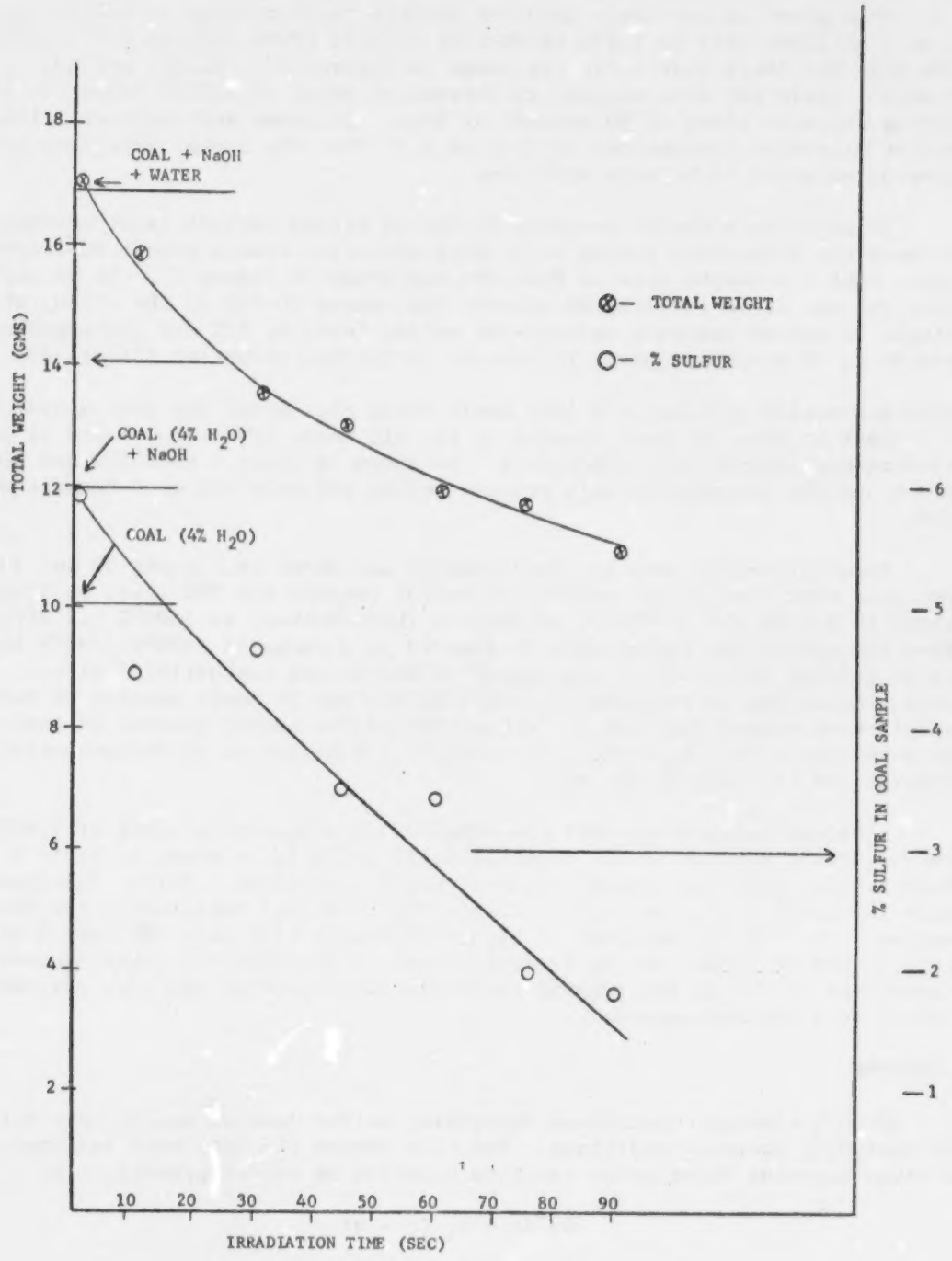

Figure 26. Sulfur reduction as a function of exposure time and water removal (PSOC-320 Pittsburgh Seam Coal, 4.5% Iron Pyrite added).

Desulfurization of Pyritic Coals Using Microwaves and Sodium Hydroxide--

This phase of the study involved pyritic coals ranging in sulfur content from 1.6% (PSOC-257) to 1.95% (PSOC-270) to 2.6% (PSOC-294) to 5.27% (PSOC-255). The data for these four coals are shown in Figures 27, 28, 29, and 30, respectively. Again the data suggest an impressive level of sulfur reduction 50-75% during exposure times of 90 seconds or less. All runs were made with 16% NaOH and at microwave frequencies of 2.45 or 8.35 GHz; the higher frequency in general appeared to be more effective.

In addition a double exposure to two 30 second periods (with washing between the exposures) proved to be more effective than a single 60 second run. Double exposure data on PSOC-294 are shown in Figure 31. It is apparent that the two steps totaling 60 seconds can remove 70-96% of the sulfur while a single 60 second exposure reduces the sulfur level by 53% and prolonged exposure to 90 seconds appears to provide no further reduction (Figure 29).

Desulfurization of Organic Sulfur Coals Using Microwaves and Sodium Hydroxide--

Work to date has been focused on Ky. #11 coals (PSOC-273, 1 and 2) and Alabama Coal Maxine Mine (PSOC-270). As shown in Table 3 PSOC-270 and PSOC-273-1 contain essentially only organic sulfur and were selected because of that.

Desulfurization data on these samples are shown in Figures 32 and 33. The data show that actual removal of sulfur reaches the 70% level as determined by Eschka and 80-85% by combustion (LECO-Method) at 1600°C (2912°F). When the combustion temperature is lowered to a range of 2600°F-2700°F there is additional reduction in the amount of registered combustible sulfur. This reduction is due to trapping of sulfur in the ash by small amounts of residual alkali thus suggesting that as much as 90% of the sulfur present in coal can be eliminated from the combustion gases by a combination of precombustion removal and trapping in the ash.

A second batch of Ky. #11 coal PSOC-273-2 contained a total of 4.64% sulfur, 2.63% pyritic, 1.87% organic, 0.14% sulfatic as shown in Table 3. Several runs were made under double exposure conditions. Sulfur analyses were made for total sulfur and sulfur forms; the total was obtained by the Eschka method. The results as shown in Figure 34 show a high rate of removal of pyritic sulfur 90-98% during exposure times of the order of sixty seconds and removal of 50-60% of the organic sulfur in corresponding exposure periods of ninety to a hundred seconds.

KINETICS

Global kinetic expressions describing sulfur removal can be very helpful in designing process conditions. For this reason the data were analyzed and plotted assuming first order reaction kinetics on sulfur present, i.e.

$$dx/dt = k_1 (a - x)$$

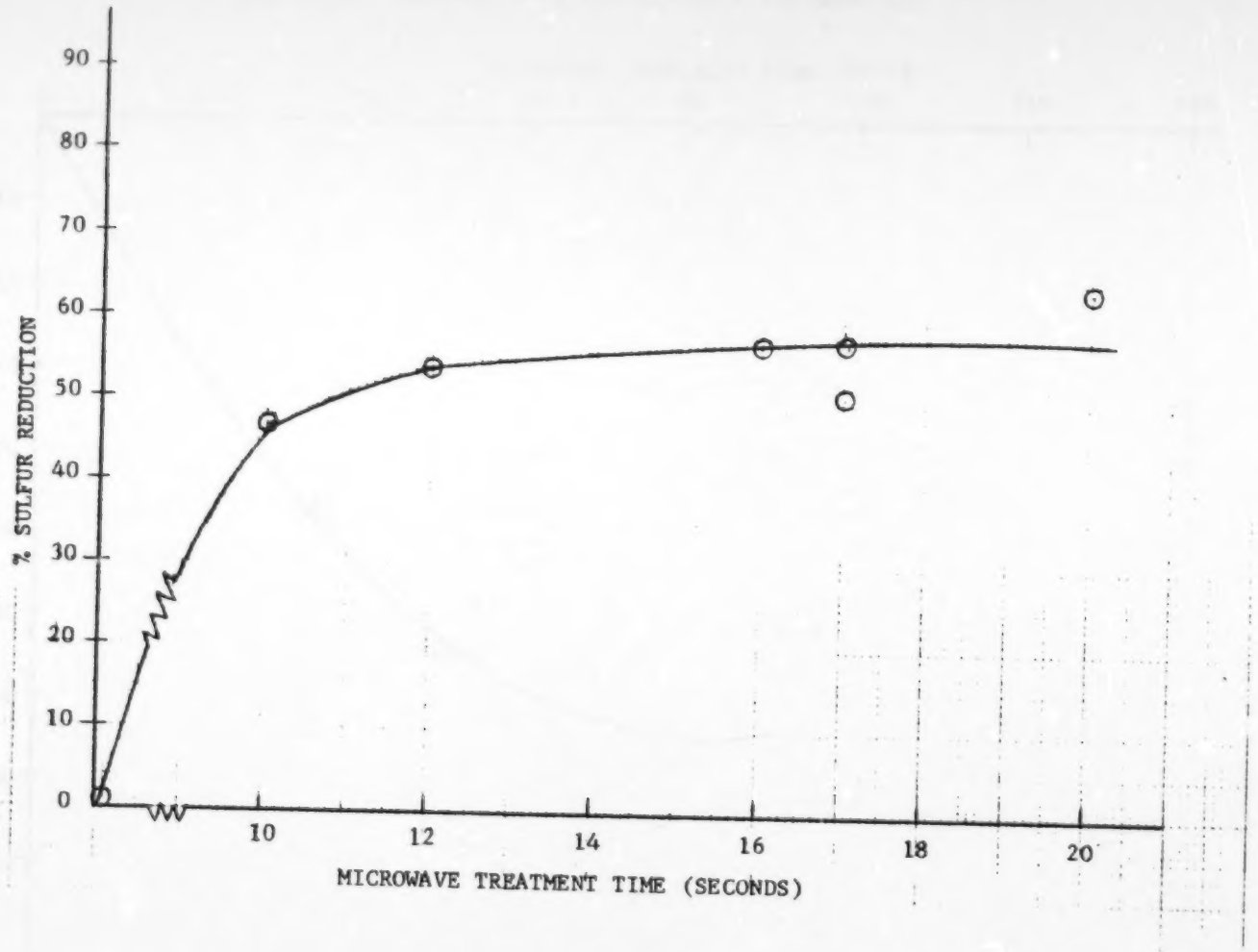

Figure 27. Reduction of total sulfur for PSOC-257.

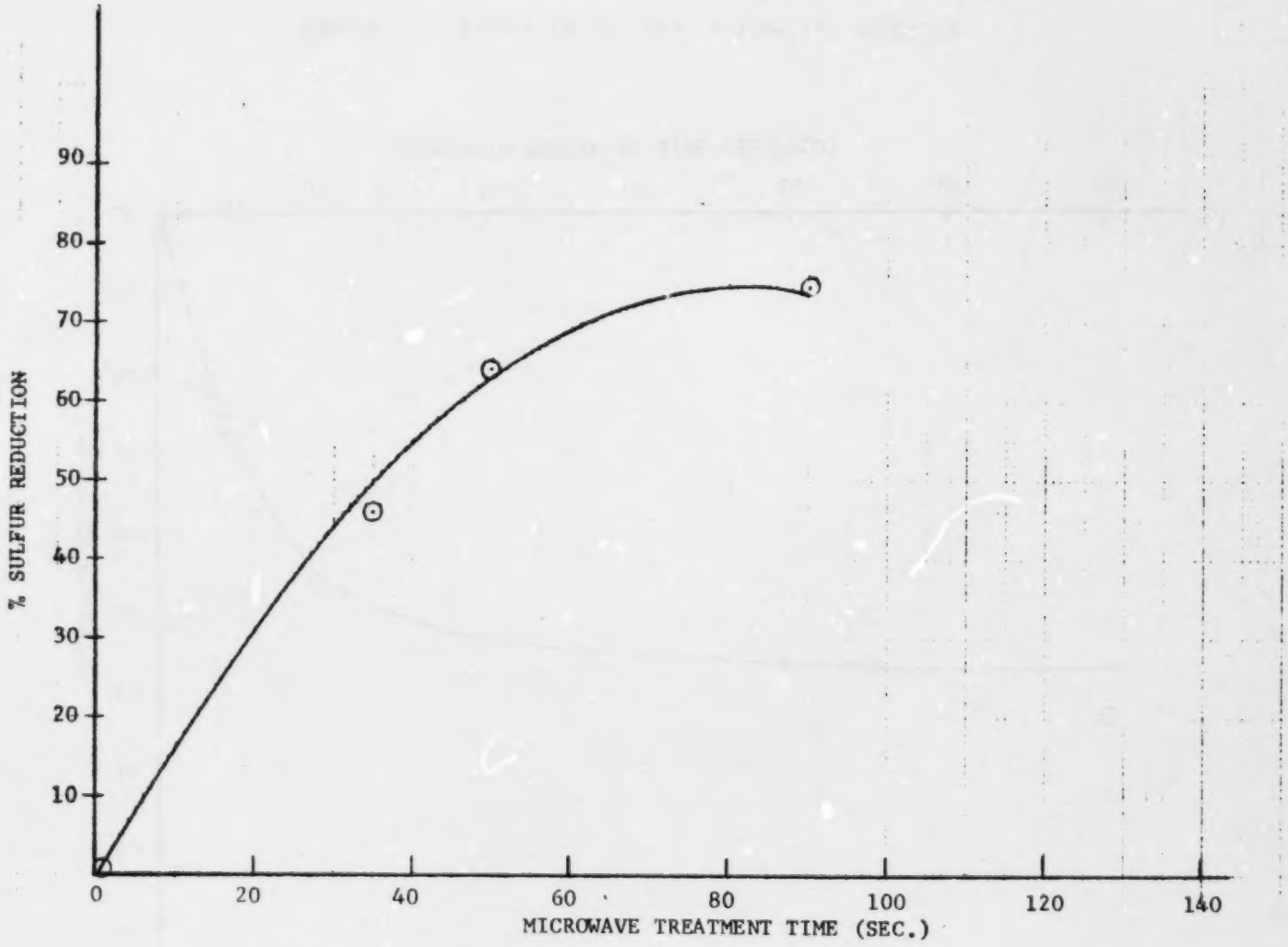

Figure 28. Reduction of total sulfur for PSOC-270.

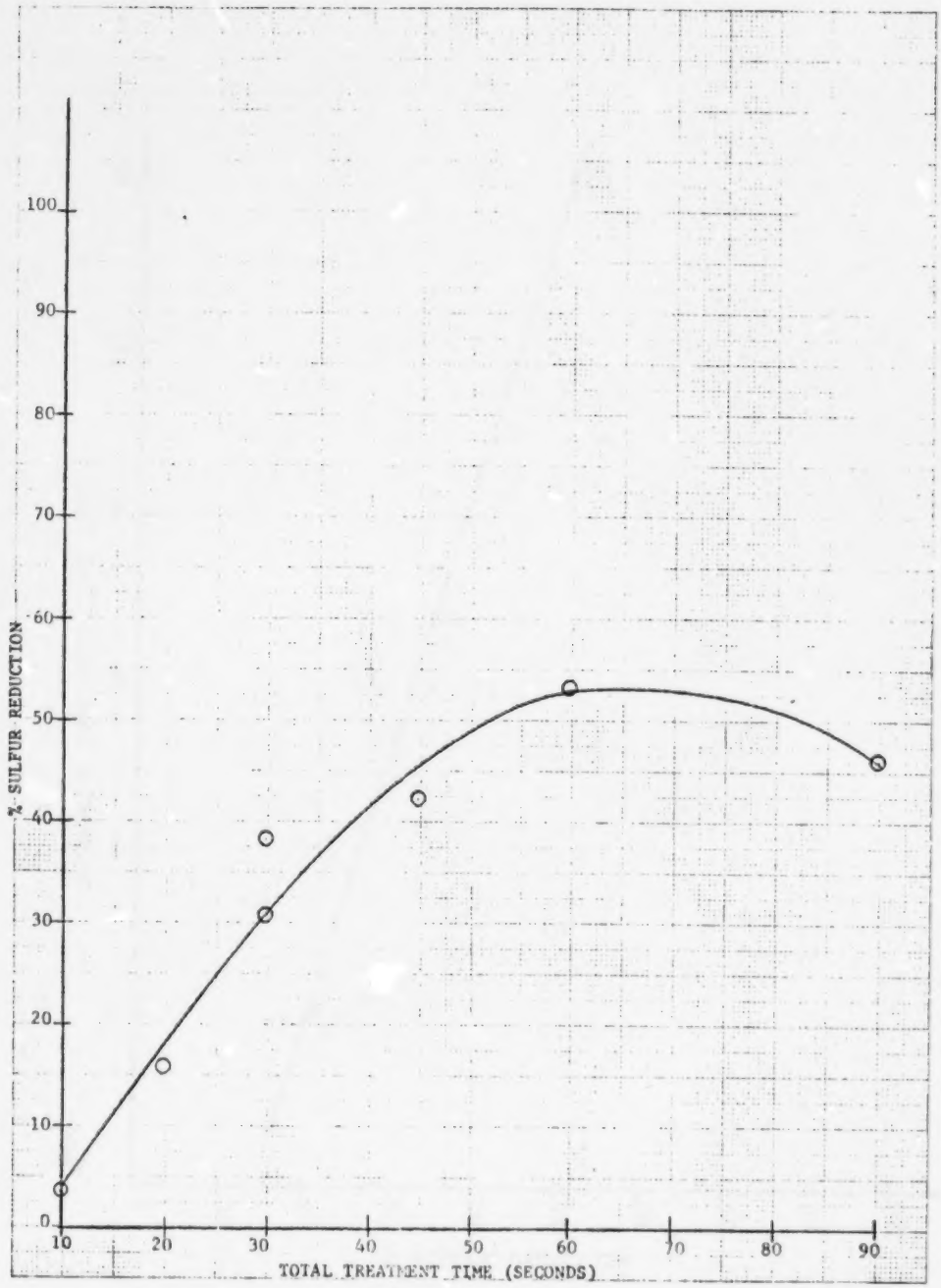

Figure 29. Reduction of total sulfur for PSOC-294.

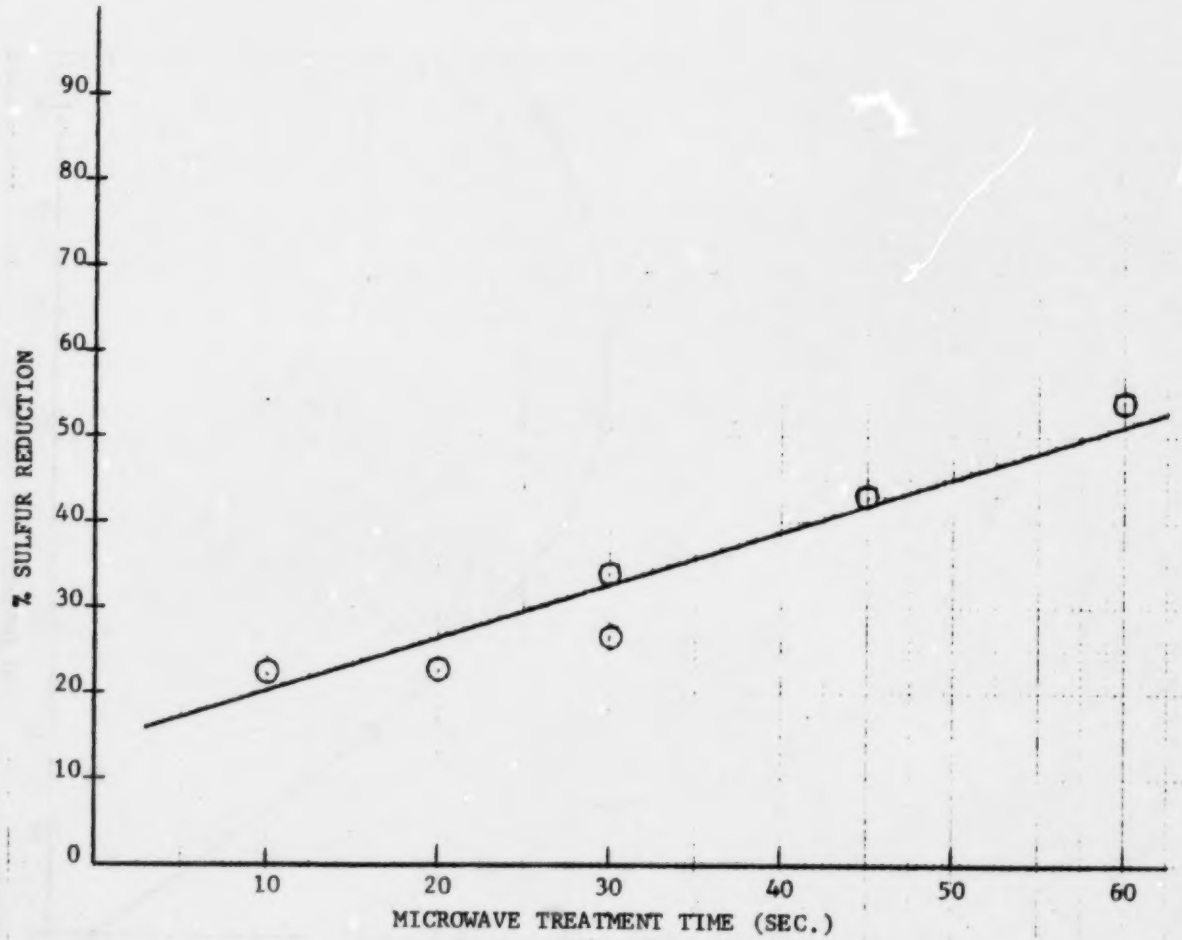

Figure 30. Sulfur reduction for PSOC-255.

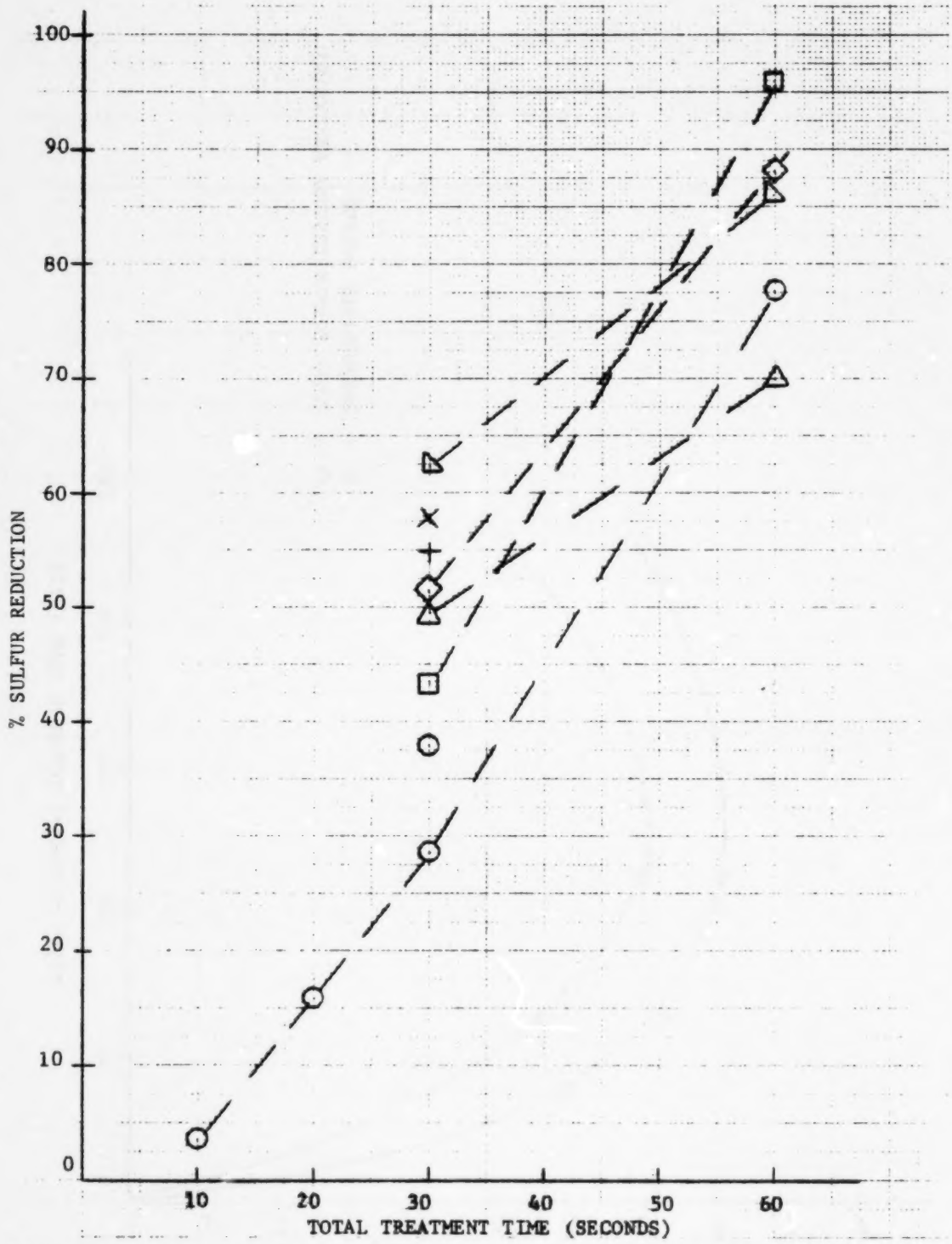

Figure 31. Time dependence of sulfur removal from coal PSOC-294 using microwave irradiation and double exposure.

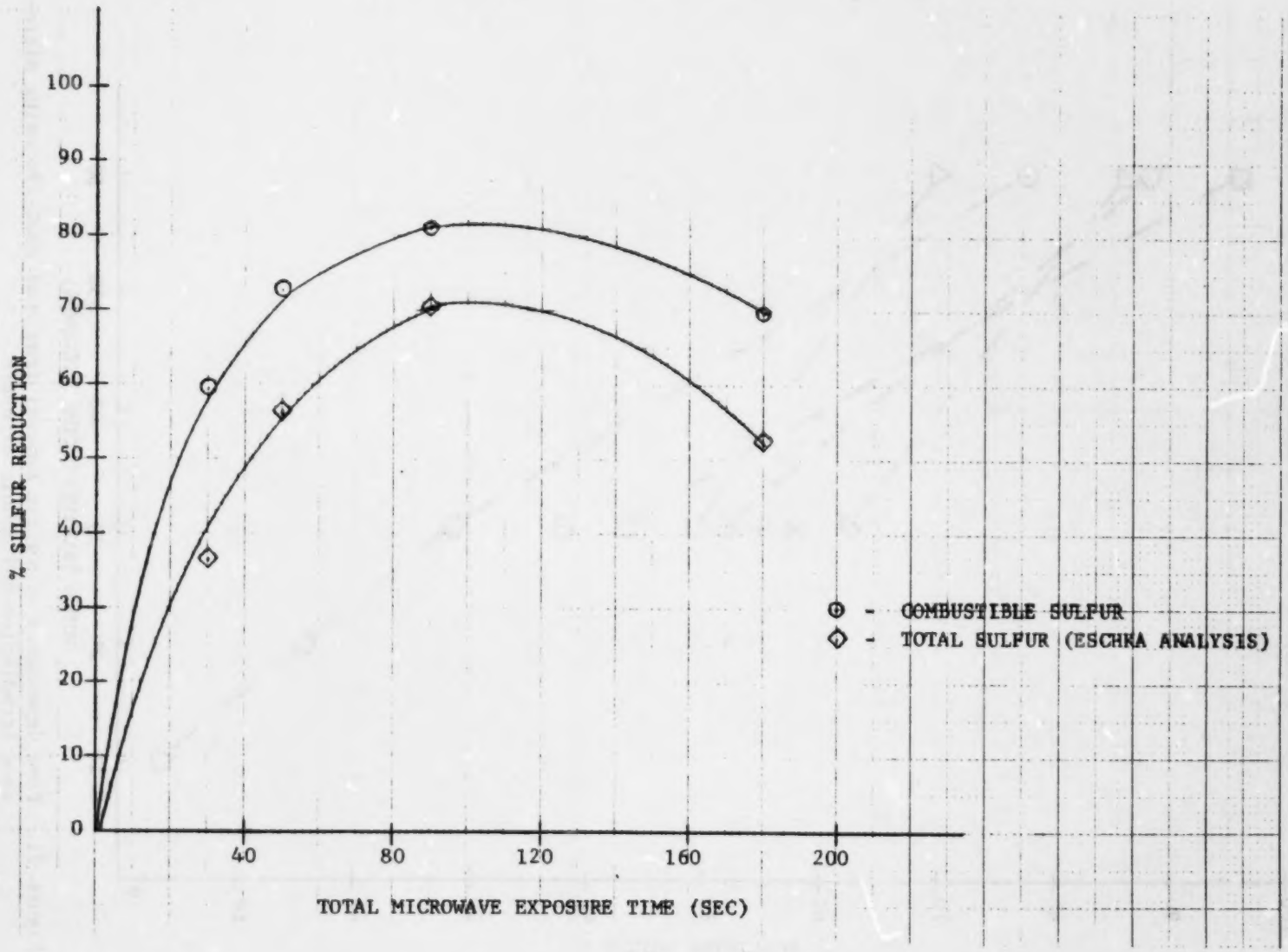

Figure 32. Reduction of total (organic) sulfur for PSOC-270, 2.45 GHz

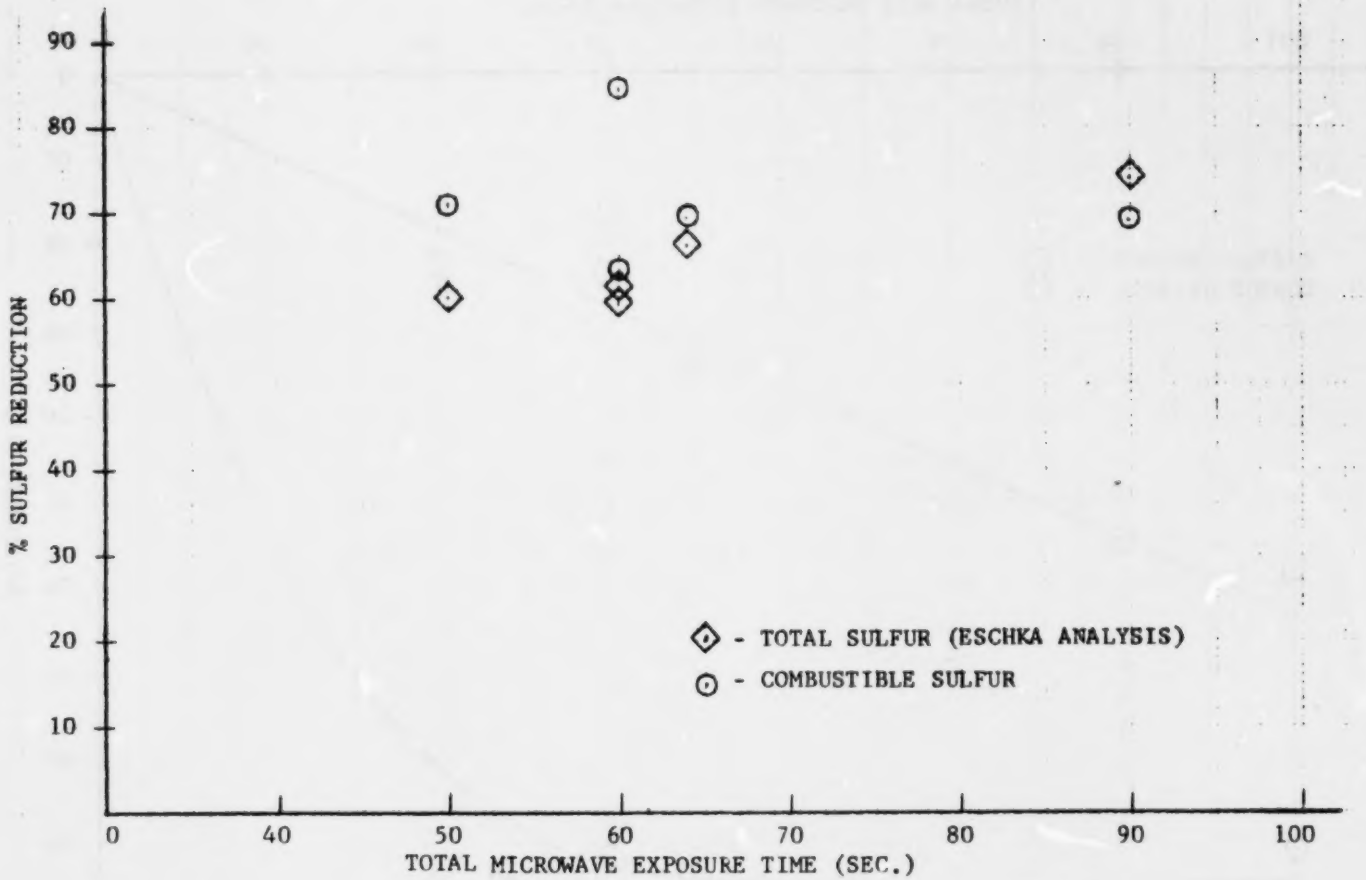

Figure 33. Reduction of total sulfur for PSOC-273-1 (double treated samples).

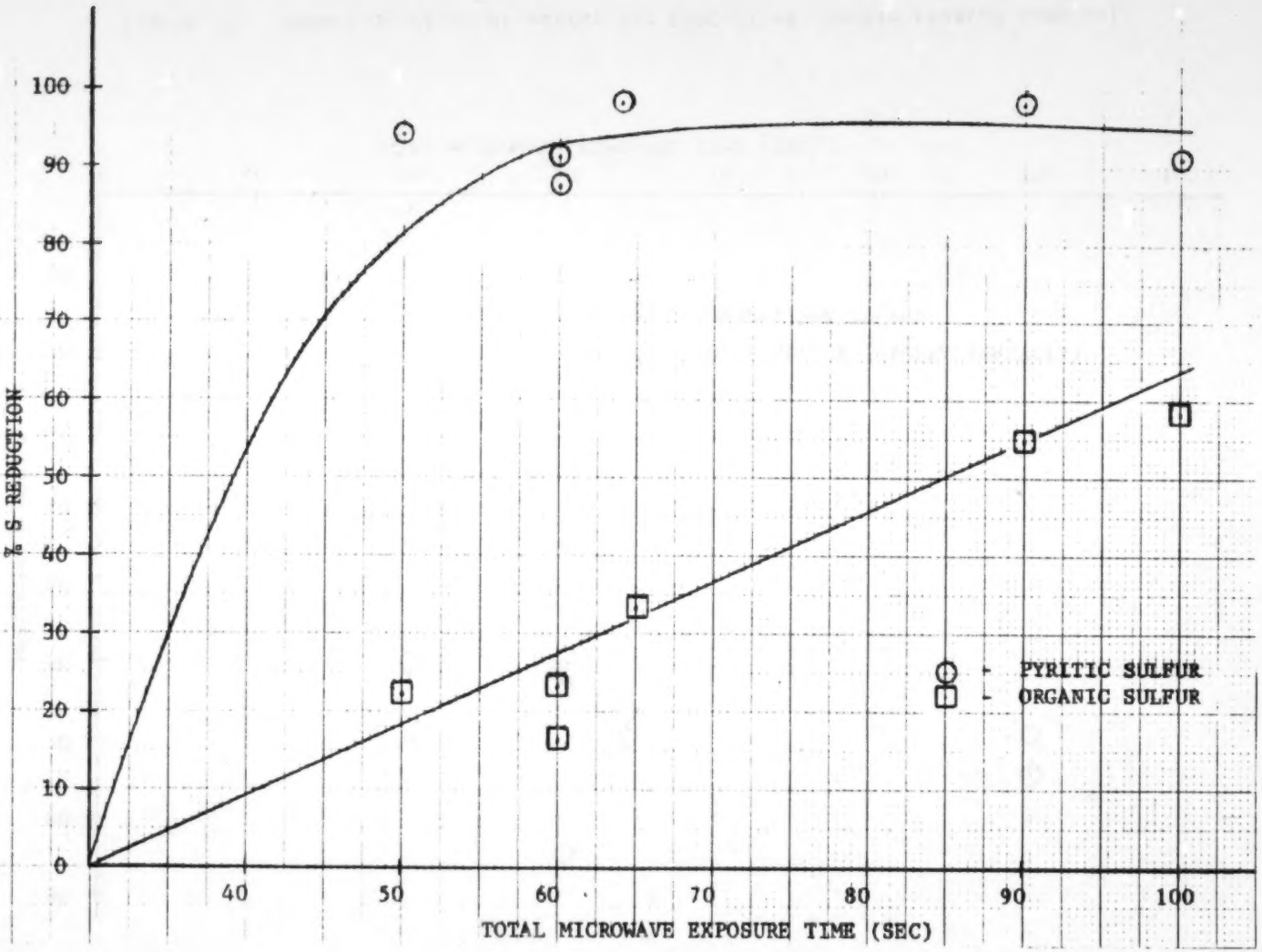

Figure 34. Reduction of sulfur forms from Ky. #11 coal (PSOC-273-2) (double treated samples).

where

a = sulfur present at time (t) = 0

$a-x$ = sulfur present after time (t)

k_1 = rate constant

Data for PSOC-294 and PSOC-255 are shown in Figures 35 and 36. The observed reasonable fit to a straight line indicates that the removal of sulfur follows first order kinetics at early times.

ASH CONTENT AND CALORIFIC VALUE OF TREATED COAL

The three coals which were extensively studied in terms of desulfurization measurements were also analyzed in terms of ash and calorific content. The results as shown in Table 6 suggest that no significant changes in either are introduced by the treatment.

Ultimate analysis was carried out on a limited basis. A typical run on PSOC-273 coal as shown in Table 7 suggests a modest increase in the oxygen content but no adverse effects on C or H.

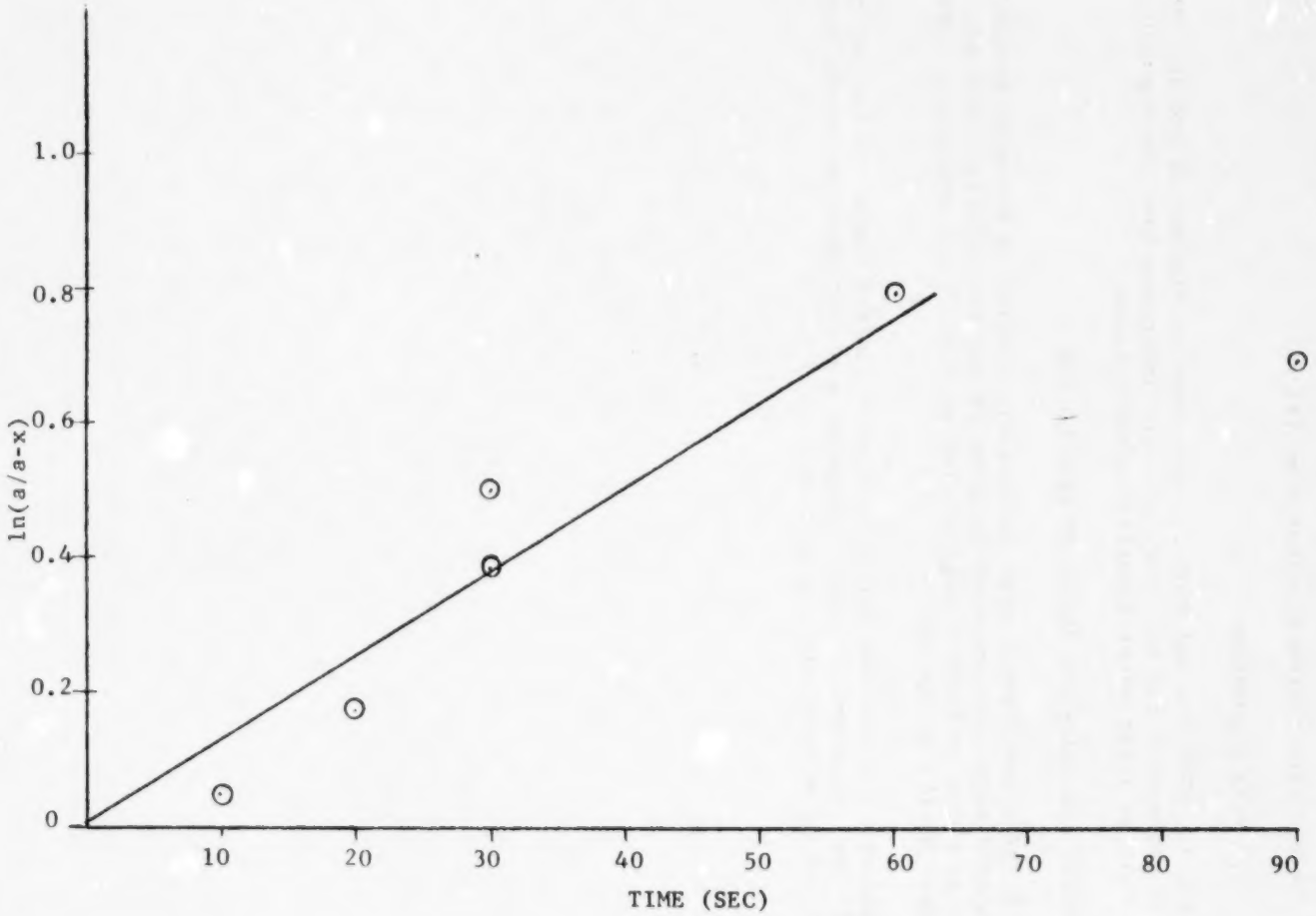

Figure 35. Sulfur removal 1st order kinetics PSOC-294.

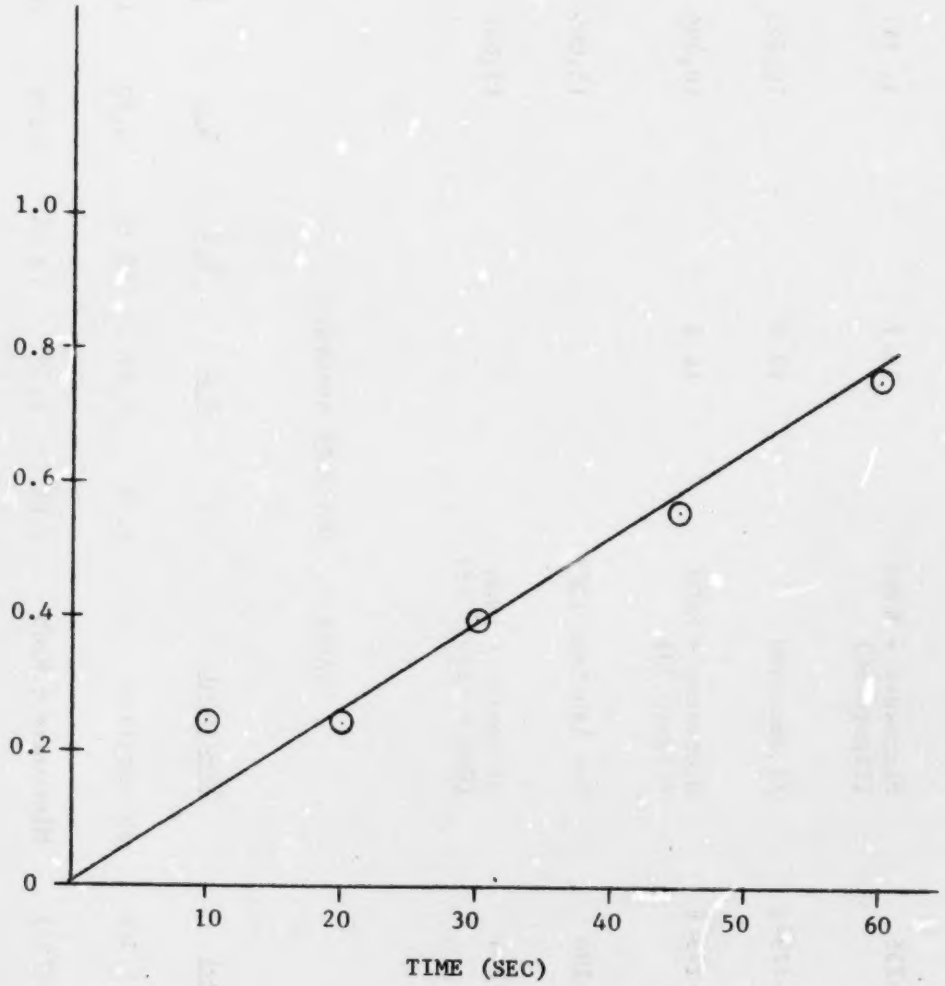

Figure 36. Sulfur removal 1st order kinetics PSOC-255.

TABLE 6. ASH AND ENERGY CONTENT

Coal	Treatment	Ash Content (% Wt.)	Calorific Value (Btu/lb)
PSOC-255	As received	17.5	11,349
PSOC-255	Microwave + NaOH (Figure 30)	18.1	11,711
PSOC-273-1	As received	12.9	10,645
PSOC-273-1	Microwave + NaOH (Figure 33)	14.3	10,395
PSOC-294	Dry Ash Free (DAF)		13,095
PSOC-294	Microwave + NaOH (DAF - Figure 29)		13,522

TABLE 7. ULTIMATE ANALYSIS

Coal	Treatment	% S	% N	% C	% H	% O
PSOC-273-1	As received	5.12	1.33	60.19	4.80	15.68
PSOC-273-1	Microwave + NaOH	1.84	1.15	63.34	4.39	20.30

SECTION 5

SCHEMATIC FLOW SHEET OF PROPOSED PROCESS

Although simplifying techniques are now being worked out, a flow diagram as shown in Figure 37 identifies the various steps in the Microwave/NaOH process.

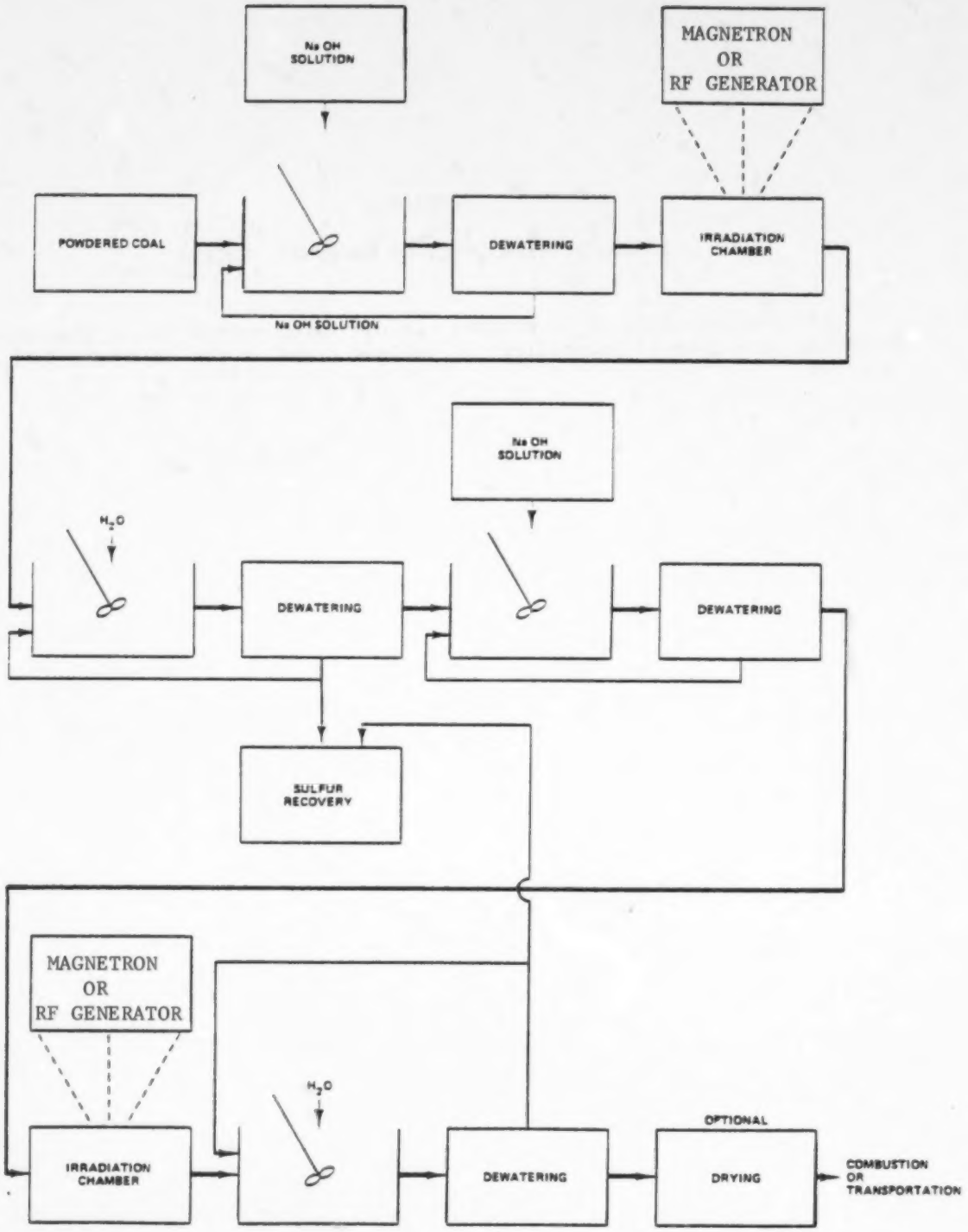

Figure 37. Proposed schematic flow sheet for G.E. chemical coal cleaning process.

SECTION 6

PROCESS ENERGY REQUIREMENTS AND ECONOMIC PROJECTIONS

The desulfurization process steps that our initial experiments have identified are:

(1) Pulverization of coal to 30-100 mesh.

(2) Mixing with a sodium hydroxide solution to produce a thick slurry.

(3) Partial drying of the slurry.

(4) Microwave irradiation for periods of 30-60 seconds at one atmosphere (N_2).

(5) Wash coal and dry for use.

(6) Convert sulfides to elemental sulfur and recover sodium hydroxide.

The last step, the sulfide conversion, may involve either the use of carbon dioxide generated by a limestone calciner step or directly from the stack gases. The carbon dioxide converts the sulfides to sodium carbonate and hydrogen sulfide; the regeneration of sodium hydroxide from sodium carbonate is accomplished by reacting it with lime, i.e.:

$$Na_2S + CO_2 + H_2O \longrightarrow Na_2CO_3 + H_2S$$

$$CaO + H_2O \longrightarrow Ca\ (OH)_2$$

$$Ca\ (OH)_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\ NaOH$$

Further steps involve the use of a Claus unit which converts hydrogen sulfide to elemental sulfur; limestone either goes to a calciner to regenerate carbon dioxide and lime

$$CaCO_3 \longrightarrow CO_2 + CaO$$

or to a landfill if stack carbon dioxide is used.

The energy required to carry out the process steps has been estimated for each individual step and is shown in Table 8 as compared to the energy content of the coal. These preliminary estimates suggest that 13-24% of the coal energy is required as input energy into the process.

TABLE 8. PROCESS ENERGY REQUIREMENTS

ESTIMATES			REMARKS
Net Coal Heat Value Loss	:	0.041 Btu Lost / Btu (Coal)	
Microwave Irradiation	:	0.08 Btu to Irradiate / Btu (Coal)	
Coal Slurry Dryers	:	0.06 Btu (Steam) / Btu (Coal)	Can Be Eliminated (Heat From Stack Gas)
Decant Liquor Evaporator	:	0.008 Btu (Steam) / Btu (Coal)	
Limestone Calciner	:	0.043 Btu (Fuel) / Btu (Coal)	May Be Eliminated
Auxiliaries	:	0.005 Btu / Btu (Coal)	
TOTAL		0.237 Btu/Btu Coal	0.134 Btu/Btu Coal*

*If Slurry Dryer and Calciner are not used.

Furthermore, economic estimates by GE-RESD, in consultation with Day and Zimmermann, Inc. (Philadelphia, Pennsylvania - Architect/Engineers), were performed on capital and operating costs for this process. The results of these economic studies are shown in Tables 9 and 10.

The calculations were based on the demand of a 500 MW coal-burning power plant, with the assumption that the desulfurization portion of the plant is on-stream 70% of the time and the pulverized coal is available at the power plant. Although these calculations can only be viewed as preliminary estimates, they do suggest however that the process has high merit and that further research and development is required.

TABLE 9. CAPITAL COSTS WITH MICROWAVE DESULFURIZATION

	DOLLARS-INSTALLED
Costs Common To Scrubbers	
• Chemical Storage & Preparation	2,800,000
• Sludge Pond	
• Railroad Siding	
Coal Washing Tanks	2,700,000
Thickeners	4,560,000
Surge Tanks	100,000
Claus (Allied)	3,865,000
Vacuum Filters	6,000,000
Pumps	100,000
Evaporators	3,040,000
Microwave Reactor (2,500 $/KW)	17,550,000
	40,715,000
Contingency (20%)	8,143,000
TOTAL	48,858,000
	97.7 $/KW

TABLE 10. OPERATING COSTS

	DOLLARS/YEAR
Electricity	1,722,000
Steam	2,260,000
NaOH	2,580,000
Lime	680,000
Operating Labor	240,000
Maintenance	2,949,400
Overhead	776,383
Taxes	1,956,000
Insurance	150,000
TOTAL OPERATING COST:	13,313,000
Amortization (20 years - 10%)	5,745,750
TOTAL ANNUAL COST	19,058,000
	.0062 $/KWH
	~$12/ton of 10^4 Btu/lb Coal

SECTION 7

CONCLUSIONS

Based on measurements and interpretation conducted in the course of this study, the following conclusions have been reached.

1. Pyrites and sodium hydroxide (with small amounts of water) absorb microwave energy much more efficiently than coal itself.

2. Microwave irradiation of pyritic coal can induce reactions between pyrite particles and their immediate environment to convert FeS_2 to FeS and produce gaseous sulfur compounds such as H_2S, COS and SO_2. This step removes about 50% of the pyritic sulfur and facilitates further removal of pyritic sulfur via physical separation techniques such as magnetic and density gradient.

3. Microwave irradiation of mixtures of coal/NaOH (16%)/H_2O (10-20%) converts pyritic or organic sulfur into water soluble sulfides (Na_2S, Na_2S_x) which can be removed from the coal by washing. The sulfides can subsequently be converted to elemental sulfur and NaOH which goes back into the process for continuous use.

4. The required microwave energy is a very modest fraction of the heat content of the treated coal ($\sim$3%) while the heat content of the treated coal remains essentially unchanged.

5. The conditions of very short exposure times (in the order of one minute) and pressure of one atmosphere required to reduce the sulfur level significantly in combination with being able to retain the heat content of the coal in combination indicate this process has great potential for economic coal desulfurization.

6. The mechanism by which fast rates of desulfurization are accomplished is most probably related to the fast (and to some degree selective) in-depth heating of the bed. The activation of water, FeS_2 and NaOH create local volatilization high temperature and pressure conditions which accelerate sulfur reactions before the coal has a chance to decompose. It is also quite possible that local non-equilibrium chemistry as a result of localized discharge sites plays a beneficial role.

7. Present economic estimates suggest that this process has economic merit as compared with other chemical desulfurization methods.

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